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THE UNIVERSITY OF ALBERTA

MASS AND CHARGE TRANSPORT BEHAVIOR OF QUATERNIZED POLYVINYLPYRIDINE MODIFIED CARBON ELECTRODES

BY

KWOK-KEUNG SHIU

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

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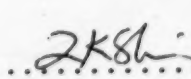

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submitted by KWOK-KEUNG SHIU
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To my family

ABSTRACT

A series of studies involving the mass transport and electron transport processes within polymer-modified electrodes have been performed. Modified electrodes sensitive to La^{3+} have been prepared by ion exchange of the electrochemically reversible anthraquinone derivatives alizarin red S (ARS) or alizarin complexone (AC) into quaternized polyvinylpyridine (QPVP) films on glassy carbon electrodes. Electrochemical and spectroelectrochemical data show that at pH 9.2 La^{3+} forms complexes with both alizarin derivatives that do not change coordination number on reduction of the ligands to the hydroquinones. Complexation of La^{3+} by polymer bound quinone occurs in the film, but the low film cation permeability results in low La^{3+} transport rates despite the presence of a coordinating ligand. Auger electron depth profiles show limited penetration of La^{3+} in the modifying film. Thin film (~30 Å) electrodes can be used to determine La^{3+} over the range 0.2 to 1 mM at pH 9.2. The analytical response arises in part from changes in transport properties in the film following complex formation. Evidence also suggests that electron hopping plays a dominant role in charge transport by ARS and AC in polycationic films. At a pH of 2 or less there is no spectroscopic or electrochemical evidence for formation of either complex. Consequently, La^{3+} complexation by the alizarin derivatives in a polymer coated electrode at pH 9.2 can be completely reversed by

transferring the electrode to a pH 2 solution. This allows the re-use of such electrodes in electroanalysis of La^{3+}.

Quaternized polyvinylpyridine film on carbon electrodes can be modified by addition of dioctylphthalate (DOP) as a plasticizer. The resulting films are more flexible, and less susceptible to dissolving in aqueous solution. Chronoamperometry shows the diffusion coefficient for charge transport by $Fe(CN)_6^{4-}$, alizarin red S and alizarin complexone in plasticized film increasing with the amount of plasticizer added although the increase varies with the redox ion examined. Plasticized QPVP-modified electrodes incorporated with alizarin derivatives respond to La^{3+} at a concentration of 20 μM.

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This thesis is also dedicated to my father, who died in 1972.

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Chapter 1 Introduction

1.1 Chemically Modified Electrodes and Their Preparation

The purpose of chemical modification of electrodes is to control the physical and chemical nature of electrode surfaces and so to control electrode reactivity or selectivity [1-2]. Chemically modified electrodes (CMEs) can be obtained by deliberately immobilizing a suitable reagent on solid phase electrodes such as C, Pt and metal oxide surfaces. The immobilized reagents are usually electrochemically active and often display chemical and electrochemical reactivities similar to those of their nonimmobilized forms. By choosing suitable reagents, direct control of the electrode surface reactivity can be achieved.

Methods used to obtain chemically modified electrodes include chemisorption, covalent bonding and polymer coating [1]. Chemisorption involves the strong or irreversible adsorption of the electroactive substance on electrode surfaces. Hubbard and Lane [3] immobilized quinone-bearing olefins on Pt electrodes in their pioneering work. Electroactive substances can also be attached to the electrode surface through reaction with chemical functionalities at the electrode. Examples include reacting

the oxide or hydroxide groups on metal oxide surfaces with a suitable organosilane reagent [4] or converting the surface carboxyl groups on an oxidized carbon electrode into amide linkages [5]. Another widely used approach is to apply polymer coatings on electrode surfaces either through electropolymerization or coating the electrode with polymer films. Electroactive functionalities can be introduced as a part of the polymer backbone or through ion-exchange of counter ions in polyelectrolyte films. Anson and coworkers [6-9] first developed chemically-modified electrodes based on ion-exchanging different metal complex anions into protonated polyvinylpyridine films. The adhesion of polymers on electrode surfaces results from chemisorption and low solubility in the contacting solution [1]. Of the three principal types of immobilization approaches, CMEs are most often prepared by chemical bonding and polymer coating. Although chemisorption involves covalent-bond-like interactions, such interactions are not always usefully stable or predictably invoked. The other approaches offer substantial synthetic diversity and can be used to attach both monomolecular and multimolecular layers on electrodes [1-2,10-14]. Generally, CMEs prepared by immobilization of electroactive reagents through chemical bonding are more durable than polymer-modified electrodes. However, multimolecular layer electroactive polymer films are technically easier to apply to electrodes than are covalently bonded monolayers. A polymer film containing a very large

number of electroactive sites (up to 10^5 monolayers) can easily be prepared and the electrochemistry is more easily observed.

1.2 Electrochemical Behavior and Kinetic Consideration of Chemically Modified Electrodes

Chemically modified electrodes have been under active research in the past few years. The development in the field has been reviewed by various authors [1-2,10-16]. A large part of the research involved basic studies of electrocatalysis [17-21] and electron-transfer kinetics [22-27]. The nature of physical phenomena governing CME behavior has been examined in detail and many characteristics are now well understood [28-34]. A chemically-modified electrode can be represented by the schematic diagram in Figure 1-1 . The surface of the electrode is modified by a film either through covalent binding or polymer coating. The modifying film may be of a monolayer or multilayers. A redox couple, P and Q, is incorporated in the film and the film is also in contact with a solution containing species A which can be electroactive or inactive. Generally, the film is swelled by the solvent molecules in the solution. Species in the solution can be brought to the film/solution interface by means of mass transport such as diffusion and mechanical stirring. Electron transfer occurs at the electrode/film

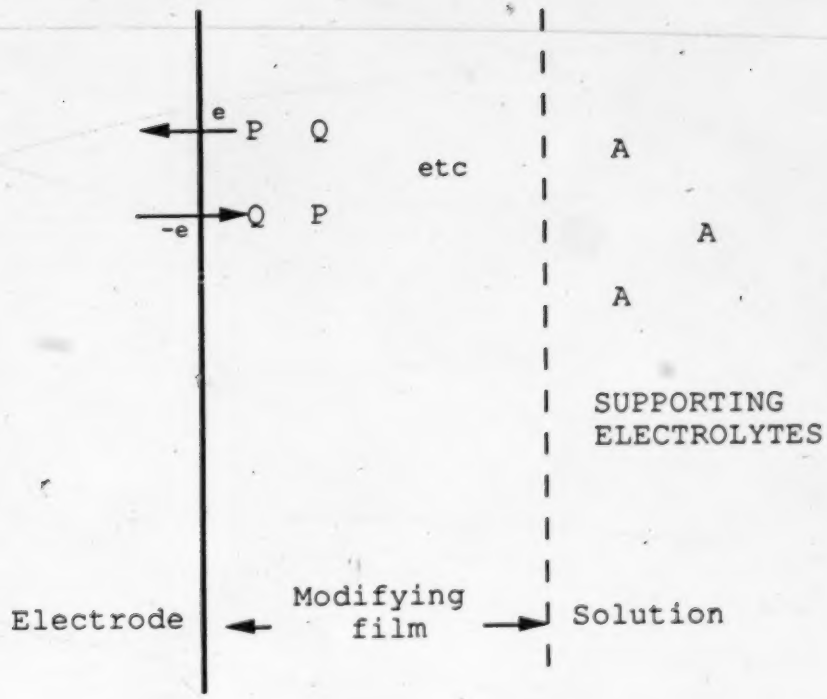


Figure 1-1. Schematic diagram of chemically modified electrode

interface. Charge can be transported through the film by exchange reactions between neighboring oxidized and reduced sites. In addition, the species present in the solution may be extracted into the film and diffuse towards the electrode/film interface. If the solution species are electroactive, charge transfer reactions may occur at one of three locations : at the solution/film interface between the species in solution and those in the film, within the bulk of the film between these species, or the solution species may react directly at the electrode/film interface.

The outcome of the kinetic behavior of such systems depends on several factors including the extraction and diffusion of solution species in the modified film, the concentration of species in solution and of the immobilized reagent in the film, film thickness and the rates of charge transfer reactions involved. These factors have been studied in great detail. The theoretical aspects of the kinetics of electrochemical reactions mediated by redox polymer films at steady state have been worked out by Saveant and coworkers [35-38], as well as others [39].

Saveant et al. [35] suggested that the kinetic behavior of such systems were controlled by four different transport processes and introduced four characteristic currents to describe the effects of each of these processes at rotating disk electrodes:

a) $i_A = FAC_A^\circ D/\delta$: current due to the transport of the substrate from the bulk of the solution to the film/solution interface, which is equal to the plateau current at a bare electrode of the same surface area,

b) $i_S = FAC_A^\circ K_D D_S/d$: current due to the diffusion of the substrate from the film/solution interface to the electrode surface, where charge transfer reactions take place,

c) $i_E = FAC_P^\circ D_E/d = FA\Gamma D_E/d^2$: current limited by the diffusion-like propagation of the electrons between the electrode/film and the film/solution interfaces, that is, through the bulk of the polymer; and

d) $i_K = FAC_A^\circ K_D k C_P^\circ d = FAC_A^\circ K_D k\Gamma$: current limited by the rate of electron cross-exchange reaction between the substrate and the active form of the attached redox couple.

The different symbols used represent the following:

C_A° is the bulk concentration of the substrate,
C_P° and Γ are the total concentration in mole/cm^3 and surface concentration in mole/cm^2 of the redox mediator in the film, respectively,
D and D_S are the diffusion coefficients of substrate in solution and in the film,

D_E is the diffusion coefficient for the diffusion-like propagation of electrons in the film,

K_D is the partition coefficient of the substrate between the film and the solution,

k is the second order rate constant of the reaction between the substrate and the active form of the mediator in the film,

A is the electrode surface area,

F is Faraday's constant,

d is the film thickness, and

δ is the diffusion layer thickness.

A theoretical model has been introduced to describe the kinetic behavior of such systems, which depends on the relative contributions of each of the four characteristic currents. There are essentially four types of kinetic behavior :

1) The electron and substrate diffusion in the film are sufficiently fast that the rate-controlling phenomenon is the catalytic reaction.

2) The catalytic reaction is sufficiently fast that the kinetics is controlled jointly by the two diffusion processes.

3) When diffusion of electrons is faster than diffusion of substrate in the film, the kinetic situation is controlled

simultaneously by the latter process and the catalytic reaction.

4) When diffusion of substrate is faster than diffusion of electrons, the kinetic situation is then controlled simultaneously by the electron diffusion and the catalytic reaction.

In addition, dimensionless parameters are introduced to give diagnostic criteria for application of the model to experimental systems. Some of the above work forms the basis for one of the methods of analysis of charge transport used in this thesis.

Ion-exchange redox polymers have been studied extensively. They are prepared by exchanging redox ions into the polymer films as counter ions. Redox anions such as $Fe(CN)_6^{3-/4-}$ and $IrCl_6^{2-/3-}$ can be incorporated into polymers that bear polycationic charges on the polymer backbone [7,19,24,28]. Protonated and quaternized polyvinylpyridine is one of the widely studied polycationic polymers. Similarly, redox cations such as $Ru(NH_3)_6^{3+/2+}$ and methyl viologen can be exchanged into Nafion [33,40-41], which is polyanionic in nature. The partition of redox ions into the polymer film depends on the partition equilibrium between ions in the film and in the solution. When a species present in a polymer film is in equilibrium with the same species in

solution, the partition equilibrium is represented by the following equation [40-42],

$$K_D = C_P/C_A \qquad (1.1)$$

where K_D is the partition equilibrium constant, C_P and C_A are the concentration of redox ions in the polymer and the concentration in the solution, respectively. The ion-exchange selectivity of these polyionic films and the permeation of substrates, neutral and charged, through such polymer films have been studied by various authors [32,43,44]. The behavior is governed by electrostatic interactions and hydrophobic interactions between the polymer and the redox ions.

In ion-exchange polymers, there are fixed charged sites on the polymer backbone. The redox ions are held in the polymer by electrostatic interactions. The charge-tranfer reactions in ion-exchange polymers are generally described by electron-hopping or site-site exchange processes between neighboring oxidized and reduced sites [8,24,30-31,45-48]. These involve the movements of the polymer chains to allow charge transport interactions between redox sites, and also the motions of charge-compensating counterions, and solvent molecules for solvation. These processes are mathematically represented by diffusion laws in which a charge transport diffusion coefficient, D_{ct}, is introduced to quantify its rate. This charge transport diffusion coefficient is

generally a function of the concentration of the redox ions in the polymer [19,24,29,47-48]. The values of D_{ct} in redox polymers are normally at least 2 to 3 orders of magnitude smaller than that in solution. In addition, this diffusion-like charge transport process limits the current attainable by these electrodes in many cases, especially when the substrate cannot permeate through the polymer film.

1.3 Analytical Aspects of Chemically Modified Electrodes

The uses of CMEs in electroanalysis has been recently reviewed [2]. Abruna [49-51] and others [52-55] have developed methods for electroanalysis of metal ions by chemically-modified electrodes. Generally, a complexing agent is immobilized at the electrode surface. The metal ions are pre-concentrated into the modified film through complexation with the bound reagents and electroanalysis follows. Cheek and Nelson [52] reported a truly remarkable detection limit for Ag(I) of about 10^{-11} M from solution using modified carbon paste electrodes. Guadalupe and Abruna [49] used 2,2'-bipyridine-bound polymer films for determination of Fe(III) in aqueous solution to 5×10^{-5} M. Baldwin et al. [53] coated carbon paste electrodes with dimethylglyoxime and used it to detect Ni(II) ions at the 50 ppb level. Even though the applications of chemically modified electrodes in

electroanalysis have provided some promising results, relatively few analytical applications of CMEs have been explored. This may result from the fact that several fundamental problems remain to be fully understood.

Problems related to mass transport effects are suggested by the following literature reports. Quaternized polyvinylpyridine modified electrodes have been used to analyze for Fe(II) and Cr(VI). However, despite the polycationic nature of the films it has been found that cationic Fe^{2+} is readily transported in protonated PVP films [55], whereas successful analysis of anionic $Cr_2O_7^{2-}$ at QPVP modified Pt electrodes required very thin films [56], suggesting transport of Cr(VI) in the film is a problem. In these two cases the coulombic interactions within the polymer do not alone provide sufficient insight into the differing behavior. A recent report by Baldwin et al. [54] shows that electrodes based on incorporating 2,9-dimethyl-1,10-phenanthroline respond to Cu(I) linearly only up to 10 μM. A report by Quadalupe and Abruna [49] suggests that the saturation of analytical responses of metal-ion sensitive electrodes may result from the change in polymer structure upon complexation and saturation can be controlled by using sufficiently thin coatings in order to provide sufficient mobility of the ligand sites for complexation. Although the thickness of the polymer-modified electrodes used for electroanalysis is not always mentioned in the literature,

the polymer films employed are usually very thin. Abruna et al. [49-51] used modified films with surface coverages from $1x10^{-11}$ to $5x10^{-10}$ mole/cm^2 (that is, up to five monolayers) for electroanalysis of different metal ions. This suggests that the permeation of substrates through the polymer films is always a problem. A study by Doublhoffer and Lange [57] provides evidence that QPVP film transport properties can be significantly affected by oxidation state changes of highly charged species such as $IrCl_6^{2-/3-}$ in the film. Some authors [58-60] have managed to improve the transport processes (electron diffusion and substrate diffusion) within the modified films by controlling the environment inside the polymer.

The analytical applications of chemically modified electrodes should be significantly expanded if some of the important factors that influence electrode performance become understood and the problems involved can be addressed. These include investigation of the nature of chemical reactions and charge transport properties within surface films, the effect of polymer permeability to substrate on electroanalytical response, the effect of saturation of the film when a substrate is present at high concentration, and the detection limits and reproducibility which can be achieved with CMEs. In our studies, we have developed polymer-modified electrodes responding to lanthanum ion (La^{3+}) based on the complexation reaction of La^{3+} with redox anions, namely alizarin red S

(ARS) and alizarin complexone (AC), confined in quaternized polyvinylpyridine (QPVP) films on carbon electrodes. This system is used as a tool to investigate different phenomena that may affect the electrode responses of these CMEs. In a separate but related project, the quaternized polyvinylpyridine film is modified by a plasticizer, dioctylphthalate (DOP), and the charge transport properties of redox anions incorporated in such films have been investigated. This leads to a better understanding of the charge transport kinetics and effects of plasticizers as well. By understanding the transport properties within these modified electrodes, the analytical system may be designed to improve the analytical performance of CMEs.

1.4 Analytical Methods Used in Studies of CMEs

In our studies, the behavior of polymer-modified electrodes involving ion-exchanging redox anions into quaternized polyvinylpyridine film is mainly investigated by electrochemical methods [61] including cyclic voltammetry (CV), differential pulse voltammetry (DPV), chronoamperometry and rotating disk voltammetry. The polymer thickness as well as the coverages of redox anions in the polymer film are measured by cyclic voltammetry. The charge transport diffusion coefficients are determined by chronoamperometry and rotating disk voltammetry. The analytical responses of

the polymer-modified electrodes are monitored by differential pulse voltammetry.

A reversible cyclic voltammogram of an immobilized redox species is shown in Figure 1-2. The peak current is expected to vary linearly with potential scan rate, υ. Integrating the total charge under the current-potential (current-time) curve gives the total quantity of attached electroactive sites [1,61]. The coverage (or the surface concentration in mole/cm^2) of the redox species is then $\Gamma = Q/nFA$. The total charge is independent of the potential scan rate. However, it is advisable to use a small scan rate in order to get an accurate measurement of the total electroactive sites in the polymer film. The thickness of the film can be calculated from the total coverage if the density of the polymer is known. Theoretical treatment of cyclic voltammetry and differential pulse voltammetry applied to redox species confined to electrode surfaces has been introduced by Brown and Anson [62]. Differential pulse voltammetry provides greater sensitivity to detect electroactivity of surface redox species, which is profitable especially when the background current is large and/or the coverage of redox species is low. The measured current is proportional to the concentration of redox species at the electrode surface.

The charge transport processes of ion-exchange redox polymers are generally described by electron-hopping and site-site exchange reactions between neighboring oxidized and

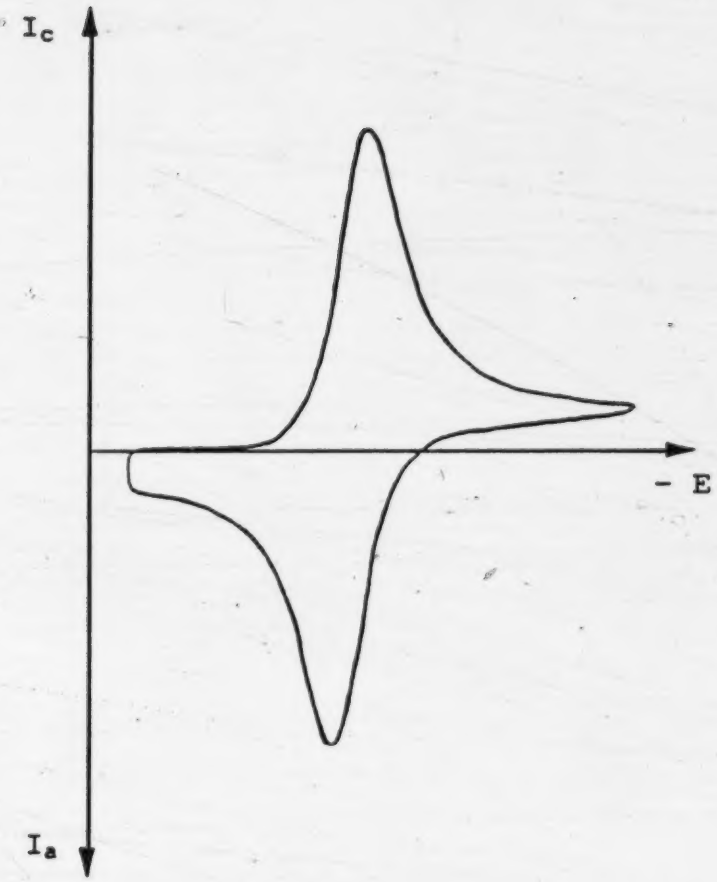


Figure 1-2. Cyclic voltammogram of redox species immobilized on a solid electrode.

reduced sites [45-48]. These processes are mathematically represented by diffusion laws in which a charge transport diffusion coefficient is introduced to measure its rate. This charge transport diffusion coefficient can be quantified by chronoamperometry, chronocoulmetry and chronopotentiometry as well as steady state methods [63-65]. The three chrono-methods have been used to measure the diffusion coefficients for electroactive anions in coatings of protonated polyvinylpyridine on graphite electrodes and their results compared [63]. The results showed that the experimental values do not depend on the method used to measure them nor upon the thickness of the PVP coatings. Charge transport diffusion coefficients of redox species at CMEs measured by steady state methods such as rotation disk voltammetry do not differ from values measured by chrono-methods in many cases.

Chronoamperometry is one of the most widely and easily used methods to measure these diffusion coefficients. The experiment is performed by applying a potential step to cause the electrochemical reaction at the electrode and the current is measured against time. Under semi-infinite diffusion conditions, that is $D_{ct}\tau/d^2 < 1$, where d is the thickness of the polymer film and τ is the experimental time scale, the decay of current should follow the Cottrell equation [1,19,30,61]

$$i = nFAD_{ct}^{1/2}C/(\pi t)^{1/2} \qquad (1.2)$$

where n is the number of electrons transferred through the redox reaction, F is Faraday's constant, A is the area of the electrode, and C is the concentration of electroactive sites in the polymer film. A plot of i *vs* $t^{-1/2}$, a Cottrell plot, should give a straight line passing through the origin. At longer times when $D_{ct}\tau/d^2 \geq 1$, the concentration profile must be described by a finite diffusion relationship and the chronoamperometric current is less than that given by the previous equation. The Cottrell plot will no longer give a straight line with zero intercept at longer times. The product $D_{ct}^{1/2}C$ can be determined from the slope of the Cottrell plot at short times after a potential step. In addition, the concentration of redox species in the polymer can be obtained from $C = \Gamma/d$. Γ is the coverage of the redox species in the polymer film, which can be determined by cyclic voltammetry. d is the thickness of the polymer film, which can be obtained from the total coverage provided that the density of the charged sites in the polymer is known, or it can be determined by profilometry. The charge transport diffusion coefficient is then obtained through calculation.

Rotating disk voltammetry has been widely used for electrocatalytic measurements at modified electrodes [1,21,66]. A stationary state is attained under such a situation and the measured current is a function of the rotation rate. The relationship can be described by the Koutecky-Levich equation [1,61]

$$1/i_l = 1/i_F + 1/(0.62nFAD^{2/3}\nu^{-1/6}\omega^{1/2}C_A) \qquad (1.3)$$

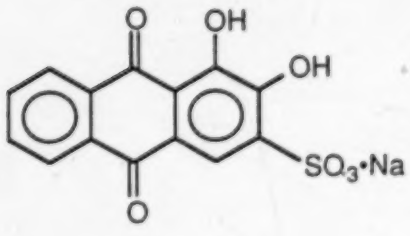
where i_l and i_F are the steady state current and "film current", respectively; n, F and A have their usual meanings, D and C_A are the diffusion coefficient and concentration of the substrate in solution, ω is the rotation rate and ν is the kinematic viscosity of the solution. A plot of $1/i_l$ *vs* $1/\omega^{1/2}$, a Koutecky-Levich plot, gives a straight line with an intercept of $1/i_F$. If i_l is limited only by the rotation dependent mass transport of the electroactive species in solution to the electrode surface, then the plot will give a straight line passing through the origin with a slope that is a function of the diffusion coefficient and concentration of the substrate. However, this is often not the case for polymer-modified electrodes. The kinetic responses are limited by one or more of the other transport processes involved and the steady state current is then controlled by the film current, especially at high rotation rate. This film current is practically the maximum current attainable at infinite rotation rate. The various dependencies of the film current can provide some information about the limiting transport processes in the polymer films, as suggested by others [35-36]. The magnitude of this film current may depend on the film thickness, loading of the electroactive species in the film, the solution concentration of the redox couple and the nature of the rate limiting process as well. When the current is limited by the charge transport reaction

through the polymer film, the film current is independent of the bulk concentration of the substrate [23,28,35-36]. According to Anson et al. [23], the limiting current arising from the diffusion-like transport of the bound reactant along the polymer chains is $i_E = nFAD_{ct}\Gamma/d^2$. In our study, a redox anion incorporated in the quaternized polyvinylpyridine modified electrode is immersed in a solution containing the same redox species. When the partition coefficient of the redox ion in the film is large, the concentration of the redox species in the film will remain nearly constant. The steady state current is measured by rotating disk voltammetry and the current reaches a plateau at high rotation rates ($\omega > 20$ rad/s). The film current is then estimated by this maximum current and is also found to be independent of the bulk concentration, which suggests that the current is limited by the charge transport reaction through the polymer. If the current is limited by this process, then $i_E = i_F$ [23,28], and the diffusion coefficient of charge transport can be calculated from

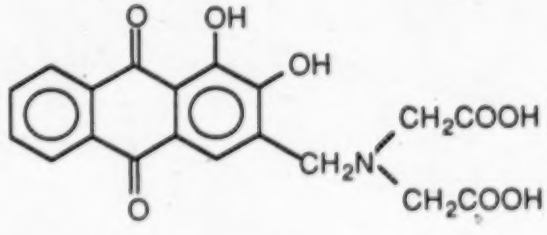
$$D_{ct} = i_E d^2/nFA\Gamma \qquad (1.4)$$

1.5 This Work

One objective of this work is to determine La^{3+}, which is not electroactive in aqueous medium under normal conditions [67]. The electroanalysis involves using electrochemically reversible anthraquinone derivatives alizarin red S (1,2-dihydroxy-9,10-anthraquinone-3-sulphonate, sodium salt; [ARS]) and alizarin complexone (3-N,N-di(carboxymethyl)-aminomethyl-1,2-dihydroxy-9,10-anthraquinone; [AC]) [68-69] as complexing agents for La^{3+}.



Alizarin red S

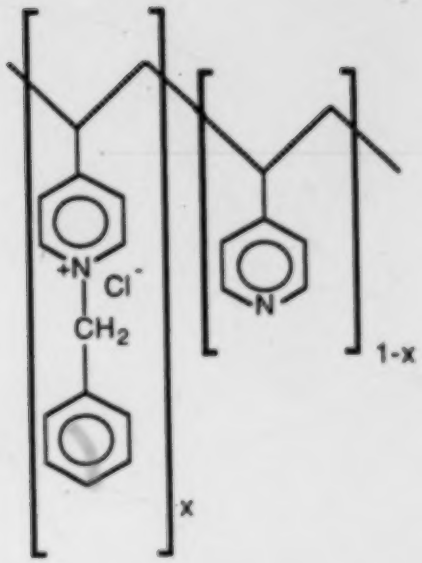


Alizarin complexone

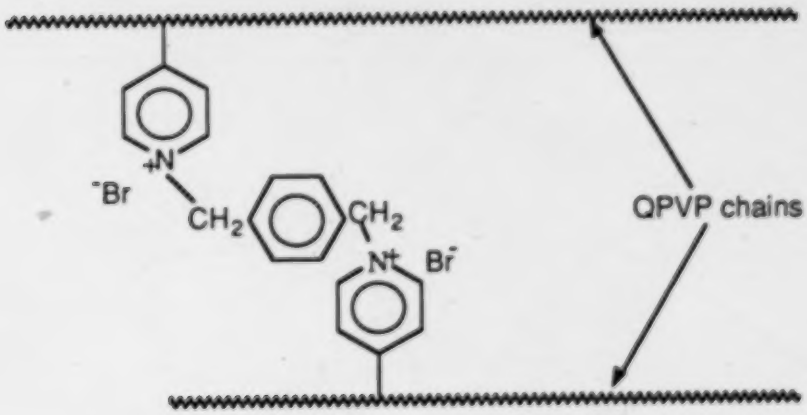
The alizarin derivatives have rich analytical metal complexation chemistry, and have been used in solution to electrochemically determine electroinactive metals [70-74], and also as colorimetric reagents for a number of metal species [75-79]. The complexation reactions between La^{3+} and the alizarin derivatives in aqueous solution have been studied both by electrochemical, colorimetric and spectroelectrochemical methods. The complexation products show a shift in reduction potential and a change in

spectrophotometric absorption maximum when compared with the alizarin derivatives themselves. We have performed a theoretical study on the effect of complex formation on the half-wave potential of redox active ligands, as presented in Chapter 2. The results are then applied to examine the complexation reactions between La^{3+} ions and the two alizarin derivatives in Chapter 3. Based on spectroelectrochemical data obtained, we conclude that the complexes between La^{3+} and the alizarin derivatives do not change their coordination stoichiometry upon reduction.

The principal aspect of this work has been to explore the properties of polymer modified electrodes that relate to the analytical application of the electrodes. Polymer-modified electrodes were prepared by ion-exchanging the alizarin derivatives into quaternized poly(4-vinylpyridine) films (QPVP), which was obtained by reacting poly(4-vinylpyridine) with benzyl chloride. The polymer films were crosslinked by reacting the unquaternized pyridine groups with crosslinking reagents, such as α,α'-dibromo-p-xylene, to improve their durability. The structures of QPVP and the crosslinked QPVP can be represented by the following schematics.



Partially quaternized poly(4-vinylpyridine) [QPVP]



Crosslinked QPVP

Responses of alizarin derivative-modified electrodes are presented in Chapter 4. Both ligands are strongly bound electrostatically within the polymer and the alizarin ions compete strongly with $Fe(CN)_6^{3-}$ for ion-exchange sites within the film. The distribution ratio (or partition equilibrium constant) measured for $Fe(CN)_6^{3-}$ is larger than those for the alizarin derivatives. However, results show that the extraction of alizarin ions into the polymer film is nearly irreversible, while polymer-bound $Fe(CN)_6^{3-}$ ions can be removed by exposing the electrode to 4M KCl solution.

The alizarin-modified electrodes show sensitivity to La^{3+} ions, as summarized in Chapter 4. Electrochemical studies and auger-electron depth profiles show that La^{3+} cannot permeate through the polymer film to a great extent despite the presence of complexing ligands in the polymer. The difficulties in permeation of the substrate limits the electroanalysis of La^{3+} with the modified electrodes. Much thinner polymer films (~ 50 Å) are necessary to offset the limitation of La^{3+} diffusion in the polymer. When thin films are used, the electrodes show an increase in current measured by differential pulse voltammetry. Linear responses to La^{3+} ion concentration are observed in a limited range (~ 0.2 to 1 mM). Since the concentrations of the ligands in the polymer do not increase, the responses must be related, at least partially, to the changes in polymer crosslinking upon complexation. In addition, evidence that suggests electron

hopping plays a dominant role in charge transport by ARS and AC in polycationic films is presented in this chapter.

In Chapter 5, the charge transport properties of plasticized QPVP films are examined. A plasticizer, dioctylphthalate (DOP), is added to the QPVP matrix. The addition of plasticizers to a polymer generally improves the flexibility and mechanical durability of the polymer [80-81]. As a result of plasticizing the film, charge transport diffusion coefficients of redox anions incorporated in these modified films are found to increase by two to five times. Applying these modified films to electroanalysis of La^{3+} can also slightly improve the electrode performance in terms of detection limit.

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Chapter 2 Effect of Complex Formation on the Half Wave Potentials of Redox Active Ligands

2.1 Introduction

The effect of complexation on the half-wave potentials of metal ions has been studied in extensive detail. Deford and Hume [1] introduced methods to determine stability constants in the case where the ligands are dissociated on reduction of the metal, and the potential shift when the coordination sphere undergoes only a partial change or no change in constituents is also well understood [2,3]. In some electroanalyses of metal ions it is the ligand, not the metal, that undergoes a redox process. For this case Casassas and Eek [4] have derived expressions for the shift in half-wave potential, $\Delta E_{1/2}$, when either the oxidized or reduced form of the ligand does not complex the metal, and shown that stability constants for the complex can be measured following an analysis that parallels the method of Deford and Hume. They did not consider the case where the ligand continues to complex the metal after the ligand undergoes a redox reaction. Florence and Belew [5] have evaluated this case for the specific situation where only a

A version of this chapter has been published. K.K.Shiu and D.J.Harrison, *J. Electroanal. Chem. Interfacial Electrochem.* 260, 249-257 (1989).

1:1 complex is formed and the stoichiometry undergoes no change following the redox reaction. In this case $\Delta E_{1/2}$ is independent of the metal-ligand concentration ratio, and is related to the ratio of the stability constants for the oxidized and reduced forms of the complex, just as is found when the metal ion is the redox site [2,3]. However, their results are not easily extended to cases where more complex equilibria are involved.

In this chapter we present a general equation for the shift in $E_{1/2}$ when a ligand that undergoes the redox reaction

$$RH_N + nH^+ + ne^- \rightleftharpoons RH_{N+n} \qquad (2.1)$$

is also involved in a series of complexation reactions involving more than one stoichiometry. The analysis is also generalized to include the case where more than one protonated form of the ligand can form a complex, and the complexes can also exist in various states of protonation. Such systems find real examples in the complexation of metals by redox active ligands with multiple acid base sites such as the alizarin derivative, alizarin complexone (AC) (3-N,N-di(carboxymethyl)-aminomethyl-1,2-dihydroxy-9,10-anthraquinone) [6,7].

List of Symbols

a_M activity of the metal ion

$K^{ox}_{i,j}$ stepwise acid dissociation constant for the oxidized form of the ligand or ligand-metal complex

$K^{R}_{i,j}$ stepwise acid dissociation constant for the reduced form of the ligand or ligand-metal complex

$\beta^{ox}_{N-i,j}$ overall pseudo formation constant for the metal ion with the N-i^{th} protonated form of the oxidized ligand

$\beta^{R}_{N+n-i,j}$ overall pseudo formation constant for the metal ion with the N+n-i^{th} protonated form of the reduced ligand

γ_H proton activity coefficient

γ_M metal ion activity coefficient

γ^{ox}_{N-i} activity coefficient of the N-i^{th} protonated form of the oxidized free ligand

γ^{R}_{N+n-i} activity coefficient of the N+n-i^{th} protonated form of the reduced free ligand

$\gamma^{ox(R)}_{i,j}$ activity coefficient of the i,j^{th} complex of the oxidized (reduced) ligand

$\alpha_i^{ox(R)}$	fraction of the i^{th} deprotonated form of the free oxidized (reduced) ligand
C_{RH}^{ox}	total concentration of the free oxidized ligand in all protonated forms
I	total current
$I_{d,c}$	cathodic diffusion limited current
$I_{d,a}$	anodic diffusion limited current
$\bar{I}_{cE}$	experimental or average Ilkovic constant for reduction of the complexes
$\bar{I}_{aE}$	experimental or average Ilkovic constant for oxidation of the complexes
$\bar{I}_{cE}'$	experimental or average Ilkovic constant for reduction of the free ligand in all protonated forms
$\bar{I}_{aE}'$	experimental or average Ilkovic constant for oxidation of the free ligand in all protonated forms

2.2 Theory

The complexation reaction of M with RH_N is represented by equation (2.2)

$$M + x\ RH_N \rightleftharpoons M(RH_{N-q})_x + xqH^+ \qquad (2.2)$$

where the charges on the metal and ligand are dropped for clarity, and N represents the number of acid sites on the ligand. The complexation equilibria involved are most easily discussed using the formulation of Casassas and Eek [4]

$$RH_N + jM \rightleftharpoons M_j{\cdot}RH_{N-q} + qH^+ \text{ (oxidized ligand)} \qquad (2.3)$$

$$RH_{N+n} + jM \rightleftharpoons M_j{\cdot}RH_{N+n-r} + rH^+ \text{ (reduced ligand)} \qquad (2.4)$$

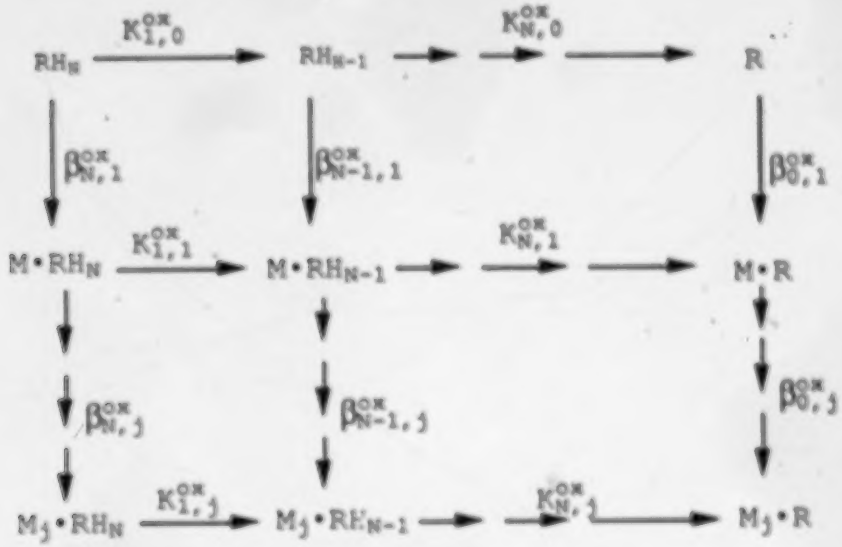
$$j = 0,\ 1,\ 1/2 \ldots 1/X$$

where the stoichiometry is formulated in terms of the fractional number of M ions involved. The factor j is given by $j = 1/x$, where x is the stoichiometric factor from equation (2.1), and X is the maximum value of coordination number of the ligand with a metal ion. Casassas and Eek [4] defined a pseudo stability constant, β, for this formulation of the stoichiometry that is related to the standard form of the stability constant β_s by

$$\beta = \beta_s \times a_{RH_N}{}^{(x-1)}\ a_M{}^{(x-1)j} \qquad (2.5)$$

where a_{RH_N} is the activity of RH_N and a_M is the activity of M. The concentrations of $M_j \cdot RH_{N-q}$ and $M(RH_{N-q})_x$ are related by $[M \cdot (RH_{N-q})_x] = x[M_j \cdot RH_{N-q}]$.

The equilibria involved in the reaction of M with the various protonated forms of RH_N are shown in Scheme I.



Scheme I

In Scheme I the i^{th}, j^{th} stepwise dissociation constant for the oxidized form of the ligand or ligand-metal complex is given by

$$K^{ox}_{i,j} = \frac{[M_j \cdot RH_{N-j}][H^+]\gamma^{ox}_{i,j}\gamma_H}{[M_j \cdot RH_{N-i+1}]\gamma^{ox}_{i-1,j}} \qquad (2.6)$$

for all values of i = 1 to N and j = 0 to 1/X. The activity coefficient of the complex of the oxidized ligand is

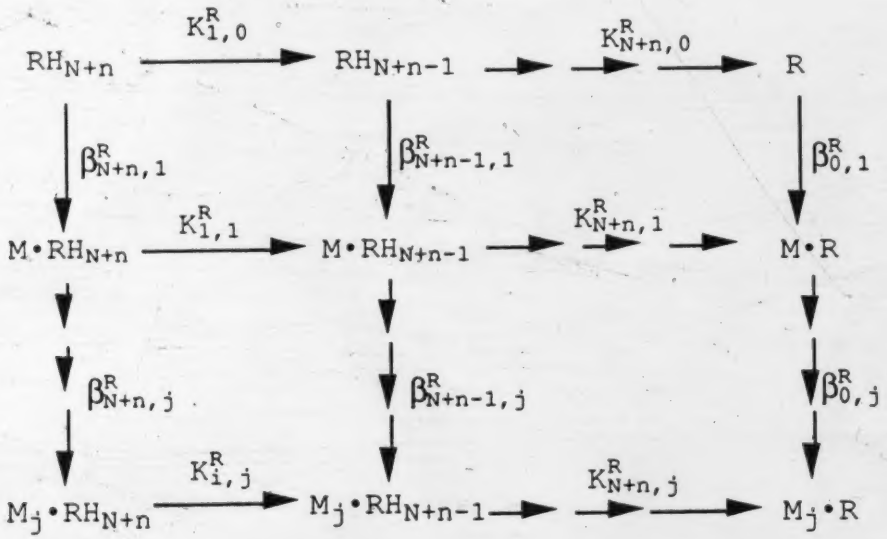
represented by $\gamma^{ox}_{i,j}$, and that for the proton by γ_H. Note that $K^{ox}_{0,j} = 1$ for all j.

The i^{th}, j^{th} overall pseudo formation constant for the complexes indicated in Scheme I are given by

$$\beta^{ox}_{N-i,j} = \frac{[M_j \cdot RH_{N-i}]\gamma^{ox}_{i,j}}{[RH_{N-i}]\gamma^{ox}_{N-i}a_M{}^j} \qquad (2.7)$$

where γ^{ox}_{N-i} is the activity coefficient for the i^{th} deprotonated form of the oxidized free ligand. The value of $\beta_{i,0}$ is defined as 1 for all i.

The equilibria involved for the reduced form of the ligand are shown in Scheme II.



Scheme II

The stepwise dissociation constants for the reduced ligand and ligand-metal complexes are defined as $K^R_{i,j}$, and are given by expressions similar to that of equation (2.6) using $\gamma^R_{i,j}$ for the activity coefficient of species involving the reduced ligand. The overall pseudo formation constant for the complexes in Scheme II is given by equation (2.8),

$$\beta^R_{N+n-i,j} = \frac{[M_j \cdot RH_{N+n-i}]\gamma^R_{i,j}}{[RH_{N+n-i}]\gamma^R_{N+n-i} a_M{}^j} \qquad (2.8)$$

where γ^R_{N+n-i} is the activity coefficient of the reduced form of the i^{th} deprotonated free ligand.

Considering the oxidized form of the ligand, the concentration of any species $M_j \cdot RH_{N-i}$ can be expressed through rearrangement of equation (2.7) as

$$[M_j \cdot RH_{N-i}] = \beta^{ox}_{N-i,j}\, a_M{}^j\, [RH_{N-i}]\, \gamma^{ox}_{N-i} / \gamma^{ox}_{i,j} \qquad (2.9)$$

Defining C^{ox}_{RH} as the total concentration of all protonated forms of the free ligand, $[RH_{N-i}]$ can be defined in terms of the fraction present of the i^{th} deprotonated species, α^{ox}_i, equation (2.10).

$$[RH_{N-i}] = \alpha^{ox}_i\, C^{ox}_{RH} \qquad (2.10)$$

The fractions α^{ox}_i are defined in terms of concentrations as is conventionally done.

$$\alpha_i^{ox} = \frac{\prod_{l=0}^{i} K_{l,0}^{ox} [H^+]^{N-i}}{\sum_{i=0}^{N} (\prod_{l=0}^{i} K_{l,0}^{ox} [H^+]^{N-i})} \qquad (2.11)$$

Substituting equation (2.10) into (2.9) and summing over all possible values of i and j gives:

$$\sum_{i=0}^{N} \sum_{j=0}^{1/X} [M_j \cdot RH_{N-i}] = C_{RH}^{ox} \sum_{i=0}^{N} \sum_{j=0}^{1/X} \beta_{N-i,j}^{ox} \alpha_i^{ox} \gamma_{N-i}^{ox} a_M{}^j / \gamma_{1,j}^{ox} \qquad (2.12)$$

Recognizing that $C_{RH}^{ox} = [RH_N] / \alpha_0^{ox}$ and rearranging equation (2.12) gives:

$$[RH_N] = \alpha_0^{ox} \frac{\sum_{i}^{N} \sum_{j}^{1/X} [M_j \cdot RH_{N-i}]}{\sum_{i}^{N} \sum_{j}^{1/X} \beta_{N-i,j}^{ox} \alpha_i^{ox} \gamma_{N-i}^{ox} a_M{}^j / \gamma_{1,j}^{ox}} \qquad (2.13)$$

A completely similar analysis leads to an expression for the reduced form of the fully protonated free ligand in terms of all species present;

$$[RH_{N+n}] = \frac{\alpha_0^R \sum_{i=0}^{N+n} \sum_{j=0}^{1/X} [M_j \cdot RH_{N-i}]}{\sum_{i=0}^{N+n} \sum_{j=0}^{1/X} \beta_{N+n-i,j}^{R} \alpha_i^R \gamma_{N+n-i}^R a_M{}^j / \gamma_{1,j}^R} \qquad (2.14)$$

where α_i^R is the fraction present of the i^{th} deprotonated form of the free reduced ligand.

The polarographic diffusion current can be expressed in terms of the cathodic process as

$$I = \bar{I}_{cE} \sum_{i}^{N} \sum_{j}^{1/X} ([M_j \cdot RH_{N-i}]_b - [M_j \cdot RH_{N-i}]) \qquad (2.15)$$

where the subscript b refers to the bulk concentration and the concentration term without subscript refers to the surface concentration at the electrode. The term $\bar{I}_{cE}$ is the average or experimental Ilkovic constant given by

$$\bar{I}_{cE} = \frac{\sum_{i}^{N} \sum_{j}^{1/X} \bar{I}_{ci,j}[M_j \cdot RH_{N-i}]}{\sum_{i}^{N} \sum_{j}^{1/X} [M_j \cdot RH_{N-i}]} \qquad (2.16)$$

where $\bar{I}_{ci,j}$ is the Ilkovic constant for the i,j^{th} species.

The diffusion limited cathodic current may be expressed as

$$I_{d,c} = \bar{I}_{cE} \sum_{i}^{N} \sum_{j}^{1/X} [M_j \cdot RH_{N-i}]_b \qquad (2.17)$$

so that

$$(I_{d,c} - I)/\bar{I}_{cE} = \sum_{i}^{N} \sum_{j}^{1/X} [M_j \cdot RH_{N-i}] \qquad (2.18)$$

The polarographic current may be described in terms of the anodic reaction by

$$I = I_{aE} \sum^{N+n} \sum_{i=0}^{1/X} ([M_j \cdot RH_{N+n-i}] - [M_j \cdot RH_{N+n-i}]_b) \qquad (2.19)$$

where $\bar{I}_{aE}$ is the average Ilkovic constant for the reduced form of the couple, and is given by an equation identical in form to equation (2.17), but referring to the reduced ligand. The diffusion limited anodic current is given by

$$I_{d,a} = - \bar{I}_{aE} \sum_{i}^{N+n} \sum_{j}^{1/X} [M_j \cdot RH_{N+n-i}]_b \qquad (2.20)$$

and so

$$(I - I_{d,a}) / \bar{I}_{aE} = \sum_{i}^{N+n} \sum_{j}^{1/X} [M_j \cdot RH_{N+n-i}] \qquad (2.21)$$

The cell potential can be expressed in terms of the concentration of free ligand using the Nernst equation,

$$E = E_R^\circ + \frac{RT}{F} \ln [H^+] \gamma_H - \frac{RT}{nF} \ln \frac{[RH_{N+n}] \gamma_{N+n}^R}{[RH_N] \gamma_N^{ox}} \qquad (2.22)$$

where E_R° is the standard half cell potential of the free ligand. Substituting equations (2.13) and (2.14) into (2.22) gives (2.23).

$$E = E_R^o + \frac{RT}{F} \ln[H^+]\gamma_H - \frac{RT}{nF} \left(\ln\frac{\gamma_{N+n}^R}{\gamma_N^{ox}} + \ln\frac{\alpha_o^R}{\alpha_o^{ox}}\right.$$

$$+ \ln \frac{\sum_i^{N+n} \sum_j^{1/X} [M_j \cdot RH_{N+n-i}]}{\sum_i^{N} \sum_j^{1/X} [M_j \cdot RH_{N-i}]}$$

$$+ \ln \frac{\sum_i^{N} \sum_j^{1/X} \beta_{N-i,j}^{ox} \; \alpha_i^{ox} \gamma_{N-i}^{ox} a_M{}^j / \gamma_{i,j}^{ox}}{\sum_i^{N+n} \sum_j^{1/X} \beta_{N+n-i,j}^{R} \; \alpha_i^{R} \gamma_{N+n-i}^{R} a_M{}^j / \gamma_{i,j}^{R}} \qquad (2.23)$$

Then from equations (2.18) and (2.21) we can write

$$\frac{\sum_i^{N+n} \sum_j^{1/X} [M_j \cdot RH_{N+n-i}]}{\sum_i^{N} \sum_j^{1/X} [M_j \cdot RH_{N-i}]} = \frac{(I - I_{d,a})\,\bar{I}_{cE}}{(I_{d,c} - I)\,\bar{I}_{aE}} \qquad (2.24)$$

When the concentration of the reduced ligand is zero initially, then $I_{d,a} = 0$, and so using equation (2.24) and recognizing that $I = I_{d,c}/2$ at $E_{1/2}$, the value of the half wave potential for the complexes, $(E_{1/2})_C$, is given by equation (2.25).

$$(E_{1/2})_C = E_R^\circ + \frac{RT}{F} \ln[H^+]\gamma_H$$

$$- \frac{RT}{nF} \left(\ln \frac{\alpha_0^R}{\alpha_0^{ox}} + \ln \frac{\gamma_{N+n}^R}{\gamma_N^{ox}} + \ln \frac{\bar{I}_{cE}}{\bar{I}_{aE}} \right)$$

$$+ \frac{RT}{nF} \ln \frac{\sum_i^N \sum_j^{1/X} \beta_{N-i,j}^{ox} \; \alpha_i^{ox} \gamma_{N-i}^{ox} a_M^j / \gamma_{i,j}^{ox}}{\sum_i^{N+n} \sum_j^{1/X} \beta_{N+n-i,j}^{R} \; \alpha_i^R \gamma_{N+n-i}^R a_M^j / \gamma_{i,j}^R} \qquad (2.25)$$

From equation (2.25) the value of $E_{1/2}$ when only the free ligand is present can be seen to depend only on the pH as a concentration dependent variable,

$$(E_{1/2})_R = E_R^\circ + \frac{RT}{F} \ln[H^+]\gamma_H - \frac{RT}{nF} \ln \frac{\alpha_0^R \bar{\bar{I}}'_{cE} \gamma_{N+n}^R}{\alpha_0^{ox} \bar{\bar{I}}'_{aE} \gamma_N^{ox}} \qquad (2.26)$$

where $$\bar{I}'_{cE} = \sum_i^N \bar{I}_{ci,0} \; [RH_{N-i}] / \sum_j^N [RH_{N-i}] \qquad (2.27)$$

and $$\bar{I}'_{aE} = \sum_i^{N+n} \bar{I}_{ai,0} \; [RH_{N+n-i}] \; / \sum_j^{N+n} [RH_{N+n-i}] \qquad (2.28)$$

The shift in $E_{1/2}$ on complex formation can then be expressed as

$$\Delta E_{1/2} = (E_{1/2})_C - (E_{1/2})_R$$

$$= - \frac{RT}{nF} \left(\ln \frac{\bar{\bar{I}}_{cE} \bar{\bar{I}}'_{aE}}{\bar{\bar{I}}_{aE} \bar{\bar{I}}'_{cE}} \right.$$

$$\left. + \ln \frac{\sum_{i}^{N} \sum_{j}^{1/X} \beta^{ox}_{N-i,j}}{\sum_{i}^{N+n} \sum_{j}^{1/X} \beta^{R}_{N+n-i,j}} \frac{\alpha_i^{ox} \gamma^{ox}_{N-i}}{\alpha_i^{R} \gamma^{R}_{N+n-i}} \frac{a_M{}^j / \gamma^{ox}_{i,j}}{a_M{}^j / \gamma^{R}_{i,j}} \right) \qquad (2.29)$$

2.3 Discussion

Equation (2.29) shows that even with complex equilibria present the shift in $E_{1/2}$ is related to the concentration of the metal, and that variation of a_M while holding the concentration of ligand constant allows evaluation of the $\beta_{i,j}$ in principle. In the common case where only one protonated form of the ligand and of the complex is significant this expression can be simplified by dropping the sum over i. As is found for the case when it is the metal that is electroactive, it is important for one species to be in excess for equation (2.29) to hold [8]. In this case, however, it is the metal ion that should be present in

excess, and this often favors formation of the one-to-one complex. When the above conditions are valid and the ratio of Ilkovic constants is assumed to be unity, as are the activity coefficients, equation (2.29) becomes

$$\Delta E_{1/2} = - \frac{RT}{nF} \ln \frac{1 + \beta^{ox}_{N-i,1} \alpha^{ox}_{i} [M]}{\sum_{j}^{1/x} \beta^{R}_{N+n-i',1} \alpha^{R}_{i'} [M]^{j}} \qquad (2.30)$$

with i not necessarily equal to i', and making no assumptions about complexation of the reduced ligand. This expression shows that $\Delta E_{1/2}$ will be constant if the stoichiometry is the same for both oxidized and reduced forms and both terms in [M] in numerator and denominator are large relative to 1. In this case the shift in $E_{1/2}$ is controlled by the ratio of the stability constant for the oxidized and reduced complex, as is found for metal centered redox systems when there is no change in the coordination shell. On the other hand, if the stoichiometry is varied by loss or gain of a ligand on reduction of the ligand $\Delta E_{1/2}$ will be constant with varying [M] only for fortuitous values of the $\beta^{R}_{N+n-i',1} \alpha^{R}_{i'} [M]^{j}$ terms. Note that the dependence of $\Delta E_{1/2}$ on pH that would occur when $i \neq i'$ is implicit in the ratio $\alpha^{ox}_{i} / \alpha^{R}_{i'}$. Equation (2.30) has been successfully applied to determine the stoichiometry of complexes formed between La^{3+} and both alizarin red S and alizarin complexone following reduction of the quinone ligand, as presented in Chapter 3 of this thesis.

The case where the coordination number changes from j to p on reduction of the ligand, and only one complex stoichiometry is important for each oxidation state, is readily derived from (2.29). Assuming the terms in [M] are large compared to one, activity coefficients are unity, and the ratio of Ilkovic constants is one, gives equation (2.31).

$$\Delta E_{1/2} = - \frac{RT}{nF} \left(\ln \frac{\beta^{ox}_{N-i,j}\ \alpha_i^{ox}}{\beta^{R}_{N+n-i',p}\ \alpha_{i'}^{R}} + (j-p)\ \ln[M]\right) \qquad (2.31)$$

This equation has the same form as that for the case where the metal ion is the redox site, except that $\Delta E_{1/2}$ varies with [M] rather than [ligand]. Again, the pH dependence is implicit in the ratio of α values when $i \neq i'$.

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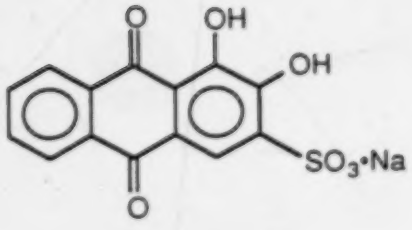
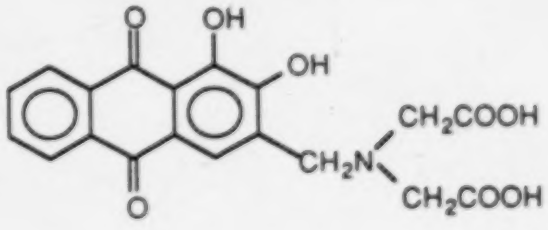
Chapter 3 Complexation Reactions Between La^{3+} and Alizarin Derivatives in Aqueous Solution

3.1 Introduction

Alizarin red S (1,2-dihydroxy-9,10-anthraquinone-3-sulphonate, sodium salt) and alizarin complexone [3-N,N-di-(carboxymethyl)-aminomethyl-1,2-dihydroxy-9,10-anthraquinone]



Alizarin red S



Alizarin complexone

and their derivatives have rich analytical metal complexation chemistry, and have been used in solution to electrochemically determine electroinactive metals and as colorimetric reagents for a number of metal species [1-21]. Alizarin complexone was first used in the colorimetric determination of fluoride ion, which was based on the formation of a ternary complex of fluoride with suitable rare-earth ions such as Ce^{3+} and La^{3+}, and alizarin complexone

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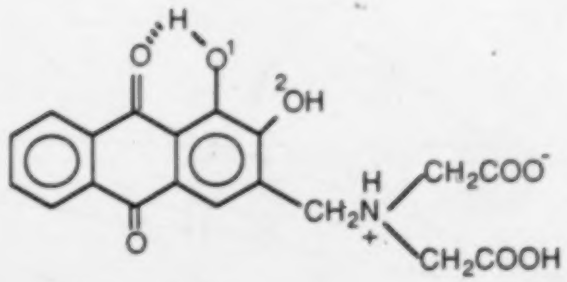
Results presented in this chapter, together with Chapter 4, have been accepted for publication in *The Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, authored by K.K.Shiu and D.J.Harrison.

[12,17]. Formation of the alizarin derivative - metal complexes results in a negative shift in reduction potential and produces a bathochromic shift of the wavelength of maximum absorption. Based on the different spectrophotometric and electrochemical properties between the free ligands and the complexes, determination of electroinactive metal ions including several of the lanthanides has been achieved [1-4,18-21].

Both alizarin red S (ARS) and alizarin complexone (AC) undergo acid-base equilibria. ARS is a sodium salt and has two acidic protons. The proton at the 2-hydroxy position is more acidic with a pK_1=7.64 and the proton at the 1-hydroxy position ionizes with a pK_2=10.95, where K_1 and K_2 are the first and second acid dissociation constants [8]. The equilibria involved in AC are more complicated. Schwarzenbach et al. [22] suggested one of the carboxyl group protons was transferred to the imino nitrogen atom during dissolution to give the following structure.



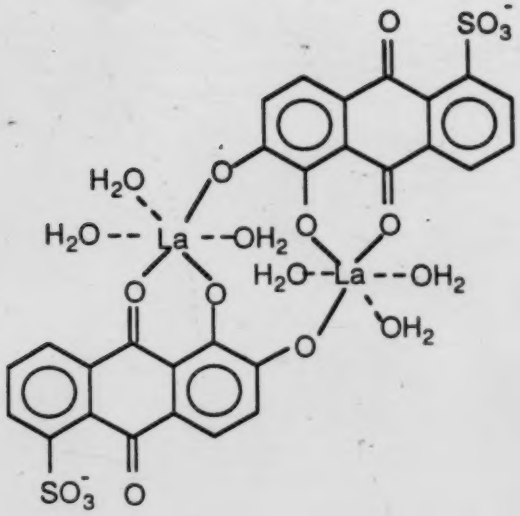
They showed that the order of dissociation of the protons was as follows: 1) the remaining carboxyl group proton; 2) the

phenolic proton in position 2; 3) the proton at the imino group and 4) the remaining phenolic proton in position 1. Ingman [23] measured the dissociation constants of AC in aqueous solution and reported the pK values of these four ionization processes as pK_1=2.40, pK_2=5.54, pK_3=10.07 and pK_4=11.98.

Reduction of alizarin derivatives involves a 2-electron reversible reduction process that results in the formation of the corresponding 9,10-diol derivatives and the two hydroxyl functionalities undergo an irreversible 2-electron oxidation [5-7,15]. Gao et al. [3] have studied the formation of Gd•ARS complex in 0.1 M ammonia buffer at pH 9.6 and suggested that the observed polarographic waves were "adsorptive complex wave". Both ARS and AC form complexes with La^{3+} that show a shift in half-wave potential, $\Delta E_{1/2}$, for the quinone reduction at the dropping Hg electrode. However, there is insufficient information in the literature concerning whether the metal complexes of the alizarin derivatives dissociate during the reduction process. Qureshi [4] reported the formation of a La•AC complex of 1:1 metal to ligand molar ratio (thought to be the 2:2 complex) at pH 4.5 and 9, and calculated a stability constant of 2.5×10^5 at pH 4.3 based on the shift of half-wave potential upon complexation, making the assumption that the complex decomposed on reduction. Others [5-6] suggested that the ARS complexes remained undissociated when reduced and our work

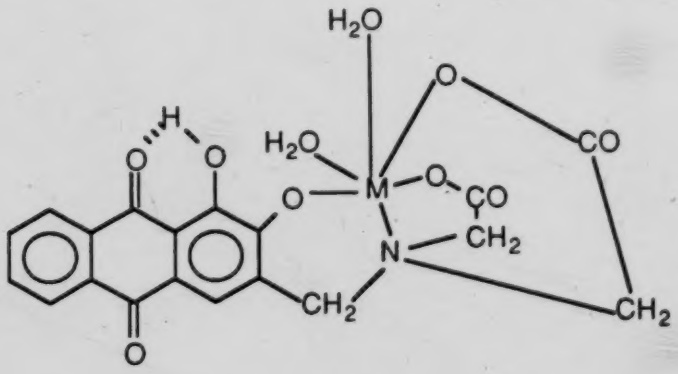
shows that this is true for both ARS•La and AC•La complexes under the conditions employed. A knowledge of the stoichiometry of both oxidized and reduced forms of the complex is important if the shift in $E_{1/2}$ is to be used to aid in identifying the metal complexed.

The structures and stoichiometries of complexes between La^{3+} and two alizarin derivatives, ARS (that is, alizarin-3-sulphonate) and alizarin-5-sulphonate, have been studied by various authors [8,10-12,16]. Tokwasheme et al. [16] reported the formation of a La•ARS_2 complex at pH 4.6. Studies by Deane and Leonard [11] on the complexation reactions between La and alizarin-5-sulphonate suggested the formation of complexes of 1:1, 1:2 and 2:2 metal to ligand ratios. For a 1:1 ARS•La^{3+} complex, La^{3+} ion may be coordinated to the hydroxyl group at position 1 and the carbonyl group at position 9, or the complex may be formed through coordination with the two hydroxyl groups [8]. The structure of a 2:2 La^{3+} to alizarin-5-sulphonate complex as proposed by Deane and Leonard [11] is shown in the following diagram. The two hydroxyl groups and the carbonyl group at position 9 were thought to participate in the complexation reaction, and the coordination around La was assumed to be octahedral.

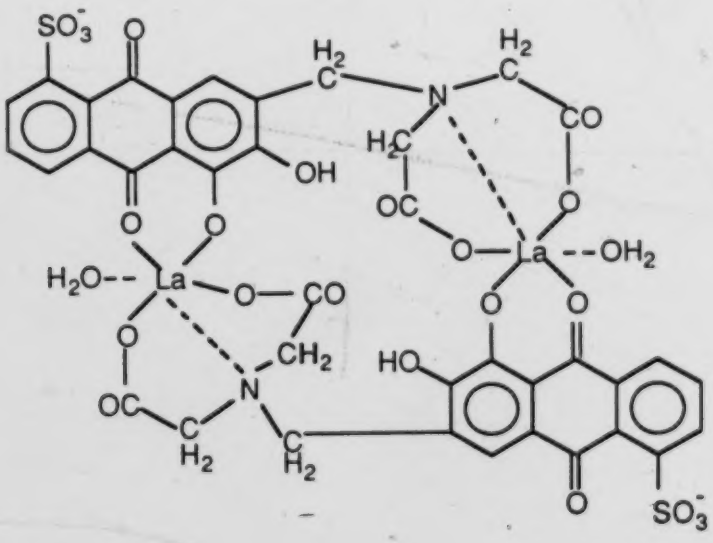


2:2 La•dihydroxyanthraquinone-5-sulphonate

The complexation reactions of AC and metal ions have been studied by different researchers [4,10-12]. Leonard and West [10] suggested that a typical 1:1 metal chelate of AC would have the following structure. The complexation involved two carboxyl oxygen's, the imino nitrogen and the hydroxyl group at position 2. The coordination around the metal was again assumed to be octahedral.



Qureshi [4], and others [12], reported the formation of a La•AC complex with a 1:1 molar ratio at pH 4.5 and suggested that it was a 2:2 complex. Langmyhr et al. [12] also found evidence for a 2:1 complex at pH values greater than 6 based on spectroscopic data. Deane and Leonard [11] performed a detailed study on the complexation between La^{3+} and 5-sulphonated-AC and suggested the formation of complexes with stoichiometries of 1:1, 2:1 and 2:2. A 1:1 ratio of the species in solution leads to the 2:2 complex as the dominant form, while the 2:1 complex becomes dominant when the metal is present in 3-fold excess or more. They have proposed a structure for the 2:2 complex. Although the coordination around the La ions were thought to be octahedral, the coordination sites of the alizarin derivative involved were different from those proposed for a 1:1 metal to AC complex.



2:2 La•sulphonated-AC

As evidenced above, there is insufficient and conflicting data concerning the structures and stoichiometries of the complexes between La^{3+} and the alizarin derivatives. However, the studies performed by Deane and Leonard [11] seem to be the most thorough and careful analysis. Based on their results, the dominance of a 2:2 La complex of alizarin-5-sulphonate and 5-sulphonated-AC is a most reasonable assumption. Since the ligands employed in this work, ARS and AC, are very similar in structure when compared with their corresponding sulphonate derivatives, the stoichiometries and structures of La•ARS and La•AC complexes are expected to be very similar to those proposed by these authors. Based on our results, the complexes remain undissoicated upon reduction. In our studies, the final goal was to incorporate the complexes in a polymer modifying film on a solid electrode, so the complexation reactions were not studied in details. However, it was necessary to determine the potential shifts of the complexes at carbon electrodes since these could differ relative to Hg due to the strong adsorption believed to occur at Hg. These questions provided the impetus for the work presented in this chapter.

Effect of Complex Formation on $E_{1/2}$

The formation and the electrochemistry of the La^{3+}, quinone complexes discussed in this chapter involves several equilibria that depend on pH and the stoichiometry of the oxidized and reduced forms of the ligand and complex. The complexation reaction of a metal, M, with the quinone, QH_N, (N = total # of acid sites on quinone Q) can be written for various stoichiometries as

$$x\ M + y\ QH_N \rightleftharpoons M_x \cdot (QH_{N-q})_y + yq\ H^+ \qquad (3.1)$$

$$x = (0,\ 1,\ \ldots,\ X)$$

$$y = (0,\ 1,\ \ldots,\ Y)$$

where x, y are the numbers of metal and ligand involved in the formation of a complex of a given stoichiometry and X, Y are the highest possible orders of complexation, and q is the number of protons displaced on formation of a given complex stoichiometry. The effect of the formal concentration of M and QH_N on shifts in the half wave potential, $E_{1/2}$, upon complex formation is analyzed in Chapter 2 using a formulation similar to that developed by Casassas and Eek [24].

The above equilibrium can be rewritten as

$$\frac{x}{y}\ M + QH_N \rightleftharpoons M_{x/y} \cdot QH_{N-q} + q\ H^+ \qquad (3.2)$$

Following Casassas and Eek [24], the pseudo formation constant for $M_{x/y}{\cdot}QH_{N-q}$ can be re-defined to include the polynucleated complex as

$$\beta^{ox}_{N-q,x,y} = \frac{[QH_{N-q}{\cdot}M_{x/y}]\gamma^{ox}_{1,x,y}}{[QH_{N-q}]\gamma^{ox}_{N-q}a_M{}^{x/y}} \qquad (3.3)$$

The analysis in Chapter 2 is still valid except that the summation should be extended to include all the complexes. The shift in half-wave potential, $\Delta E_{1/2}$, for the ligand in the presence of the metal is then

$$\Delta E_{1/2} = (E_{1/2})_C - (E_{1/2})_R$$

$$= -\frac{RT}{nF}\left\{\ln \frac{\bar{I}_{cE}\bar{\bar{I}}'_{aE}}{\bar{\bar{I}}_{aE}\bar{I}'_{cE}}\right.$$

$$\left. + \ln \frac{\sum_{i}^{N}\sum_{x}^{1/X}\sum_{y}^{1/Y}\beta^{ox}_{N-i,x,y}}{\sum_{i}^{N+n}\sum_{x}^{1/X}\sum_{y}^{1/Y}\beta^{R}_{N+n-i,x,y}} \frac{\alpha^{ox}_{i}\,\gamma^{ox}_{N-i}}{\alpha^{R}_{i}\,\gamma^{R}_{N+n-i}} \frac{a_M{}^{x/y}}{a_M{}^{x/y}} \frac{/\gamma^{ox}_{1,x,y}}{/\gamma^{R}_{1,x,y}}\right\} \qquad (3.4)$$

where R, T and F have their usual meanings. The other symbols are defined in Section 2.1 of Chapter 2. When only one protonated form of the ligand, and oxidized and reduced forms of the complex are significant, and only the 2:2 complex is dominant for the oxidized ligand-metal complex, then equation (3.4) becomes

$$\Delta E_{1/2} = -\frac{RT}{2F}\ln \frac{1 + \beta^{ox}_{N-i,1,1}\,\alpha^{ox}_{i}\,[M]}{\sum_{x}^{1/X}\sum_{y}^{1/Y}\beta^{R}_{N+2-i',x,y}\,\alpha^{R}_{i'}\,[M]^{x/y}} \qquad (3.5)$$

where the ratio of Ilkovic constants and activity coefficients are assumed to be unity. The α_i^{ox} and $\alpha_{i'}^{R}$ are the fraction of the i^{th} and i'^{th} deprotonated forms of the quinone and hydroquinone derivatives, respectively. The term $\beta_{N-i,x,y}^{ox}$ is the overall pseudo formation constant for the x:y complex of the oxidized form of the ligand, as defined in equation (3.1). The term $\beta_{N+2-i',x,y}^{R}$ is the overall pseudo formation constant for the x:y complex with the i'^{th} deprotonated form of the reduced ligand. The use of this formulation is described in Chapter 2 and follows that introduced by Casassas and Eek [24]. Note that when formation of the oxidized form of the complex is significant the condition $\beta_{N-1,1,1}^{ox}\alpha_i^{ox}[M] >> 1$ will hold. From a study of the effect of [M] on $\Delta E_{1/2}$ at constant quinone concentration it is possible to determine if the coordination number of the complex changes on reduction of the quinone. A similar but less general analysis has been presented by Florence and Belew for the case where only one complex stoichiometry is considered [25].

3.2 Experimental

Alizarin red S and alizarin complexone were used as received (Aldrich). Water was doubly distilled from alkaline permanganate. All other chemicals were reagent grade.

Trifluoroacetate buffer (pH 2) and acetate buffer (pH 4) were prepared by adjusting the pH of a 0.1 M solution of the corresponding acid with KOH or NaOH to the desired pH values. Phosphate buffers were obtained from a solution of 0.1 M in each of NaH_2PO_4 and Na_2HPO_4, and the pH was adjusted by addition of NaOH. An ammonia buffer was prepared by adjusting the pH of a solution containing 0.1 M NH_4Cl and 0.1 M NH_4OH to 9 or 9.2 with HCl.

Glassy carbon rods (Atomergic Chemetals, N.Y.) were sealed in teflon sleeves, polished with alumina (Beuhler) to a 1 μm final polish, and rinsed in water in an ultrasonic bath for 2 to 5 min. Ultrasonicating was used to remove residual alumina left on the electrode after polishing. Only trace amounts of alumina left on an electrode would result in additional reduction peaks for the alizarin derivatives when studied by electrochemical methods, due to adsorption of redox species. A dropping mercury electrode was also used as the working electrode in some cases. Potentials were measured with respect to a KCl-saturated calomel electrode (SCE).

Cyclic voltammetry was performed with a Pine Instruments RDE-4 Potentiostat and a Kipp and Zonen BD90 X-Y recorder. A PAR 174A Polarographic Analyzer and Houston Instruments X-Y recorder were used for differential pulse (DP) voltammetry, with a scan rate of 1 mV/s, modulation amplitude of 5 mV and 0.5 s drop time.

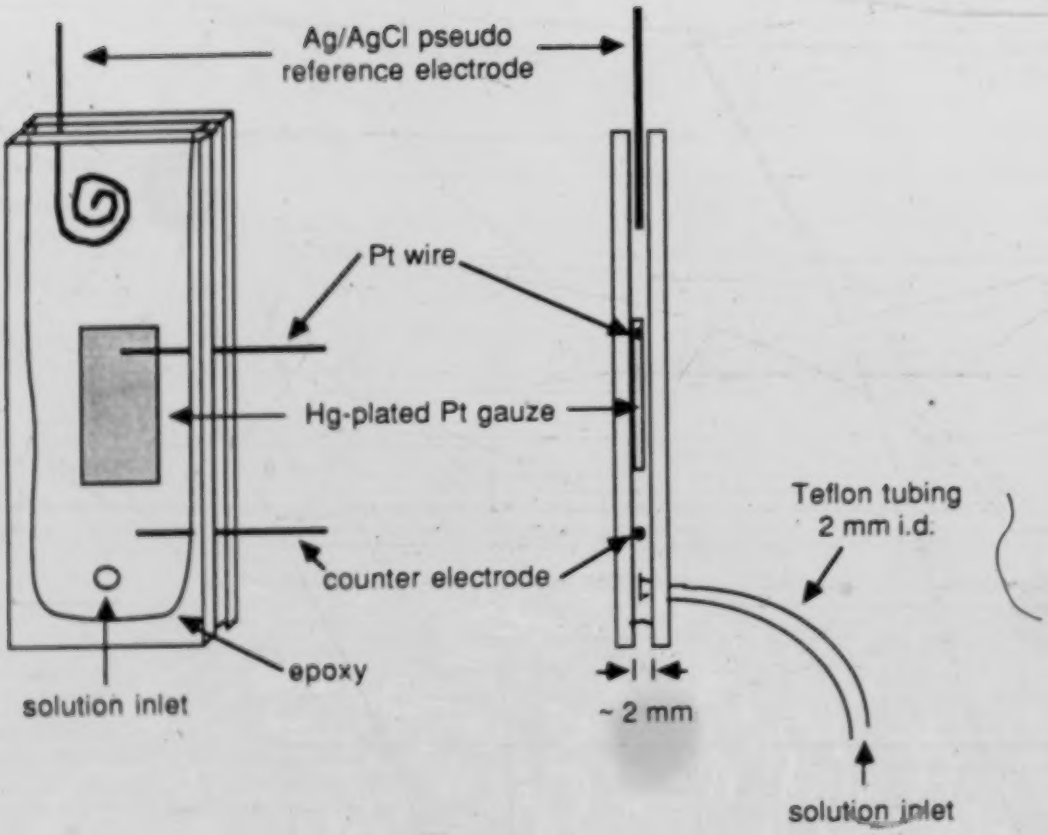
Absorption spectra of solutions were recorded by a Hewlett-Packard 8450A UV-Vis photodiode array spectrometer and concentrations of the alizarin derivative used were usually between 0.1 and 1 mM. The composition of complex was determined by the continuous variation method. A series of solutions containing different molar ratios of La to alizarin derivative, with a total concentration of 1 mM in 0.1 M ammonia buffer at pH 9.2, was prepared. The absorption spectra were recorded and the absorption at a selected wavelength was plotted against the molar fraction of the alizarin derivative The composition of the complex was obtained from the intersection of two linear portions of this plot.

Studies of the shift in half-wave potential, $\Delta E_{1/2}$, of the redox ions upon complexation were performed by differential pulse voltammetry. An appropriate amount of La^{3+} solution was added to a solution containing one of the alizarin derivatives in ammonia buffer of pH 9.2 and the mixture was diluted with the buffer to give a solution with an alizarin concentration of 20 μM. The concentration range

of La^{3+} solutions was between 30 and 100 μM. The reduction peak potential was determined from the differential pulse voltammogram. The shift in half-wave potential was assumed to be the same as the shift in reduction peak potential, which is valid when reversible or quasireversible behavior is observed.

A thin layer spectroelectrochemical cell was prepared by sealing with epoxy (Clear-Hysol) a Hg plated Pt gauze (80 mesh, Johnson-Matthey) working electrode, Pt counter electrode, and Ag/AgCl pseudo reference electrode, between two microscope slides. The working electrode (1 cm x 1.5 cm) was prepared by applying a potential of ~ -1.0 V *vs* SCE to a Pt gauze, in a solution containing 1 mM $Hg(NO_3)_2$ and 0.1 M KCl, for 15 min and then it was rinsed with distilled water. The Ag/AgCl pseudo reference electrode was obtained by placing a Ag wire in a 0.5 M KCl solution at a potential of 0.3 V for 15 min. A schematic diagram of the spectroelectrochemical cell is shown in the following. Deaerated solution containing 0.2 mM of the alizarin derivative in 0.1 M ammonia buffer (pH 9.2) and the appropriate amount of La^{3+} was introduced through a hole drilled in one of the slides at the bottom of the cell, which was sealed with electrical tape, and the top of the cell was then sealed with Parafilm. The cell, with a path length of about 2 mm, was placed in a Hewlett-Packard UV-Vis photodiode array spectrometer and spectra were recorded every

2 min for 30 to 40 min. Reductions were usually complete by 15 to 20 min as evidenced by obtaining a constant spectrum.



Schematic diagram of a thin layer spectroelectrochemical cell

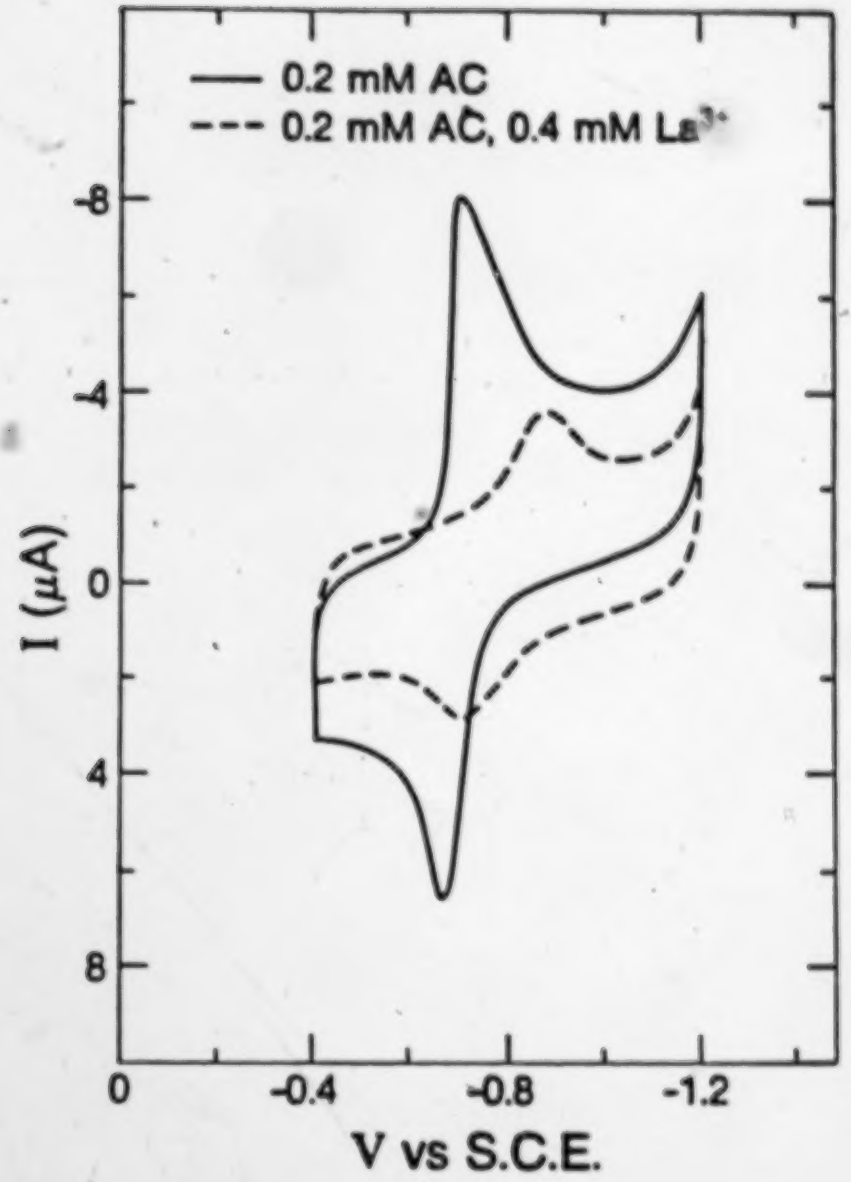
3.3 Results and Discussion

Both cyclic voltammetry and differential pulse voltammetry have been used to study the complexation reactions between the alizarin derivatives and various lanthanide ions (Ln^{3+}) including La^{3+}, Nd^{3+}, Gd^{3+} and Yb^{3+} at mercury electrodes. The solutions contained a lanthanide to quinone ratio of 1 to 2, and were buffered at about pH 9, either with 0.1 M NH_4Cl/NH_4OH or Na_2HPO_4/NaH_2PO_4 buffers. The charge is 2^- for ARS, and about 80% 2^- and 20% 3^- for AC at pH 9 [8,23,26]. At higher pH's, lanthanide ions are involved in hydrolysis reactions and precipitates are formed [26]. Results of differential pulse voltammetry at mercury show that the alizarin derivatives reduce at ~ -0.67 V *vs* a KCl-saturated calomel electrode (SCE). On addition of Ln^{3+} ions, the peak current of the free ligands decreases and an additional peak corresponding to the formation of the complex appears at more negative potentials. By comparing the relative magnitudes of these two peaks, information about the relative stability of the Ln•Q complexes can be obtained. In ammonia buffer, the reduction peak corresponding to the complex of La•Q is much larger than that resulting from the reduction of the free ligand, while the reduction of the free ligand is predominant in a solution containing Yb^{3+} and the alizarin derivative. This indicates that complex formation is favored for the lighter lanthanides in ammonia buffer. On the other hand, formation of a complex between the ligands

and heavier rare-earth metals is more favorable in phosphate buffer. This suggests that the buffer itself plays a role in the complexation reactions and may result in selective determination of different lanthanide ions. However, this effect was not further explored.

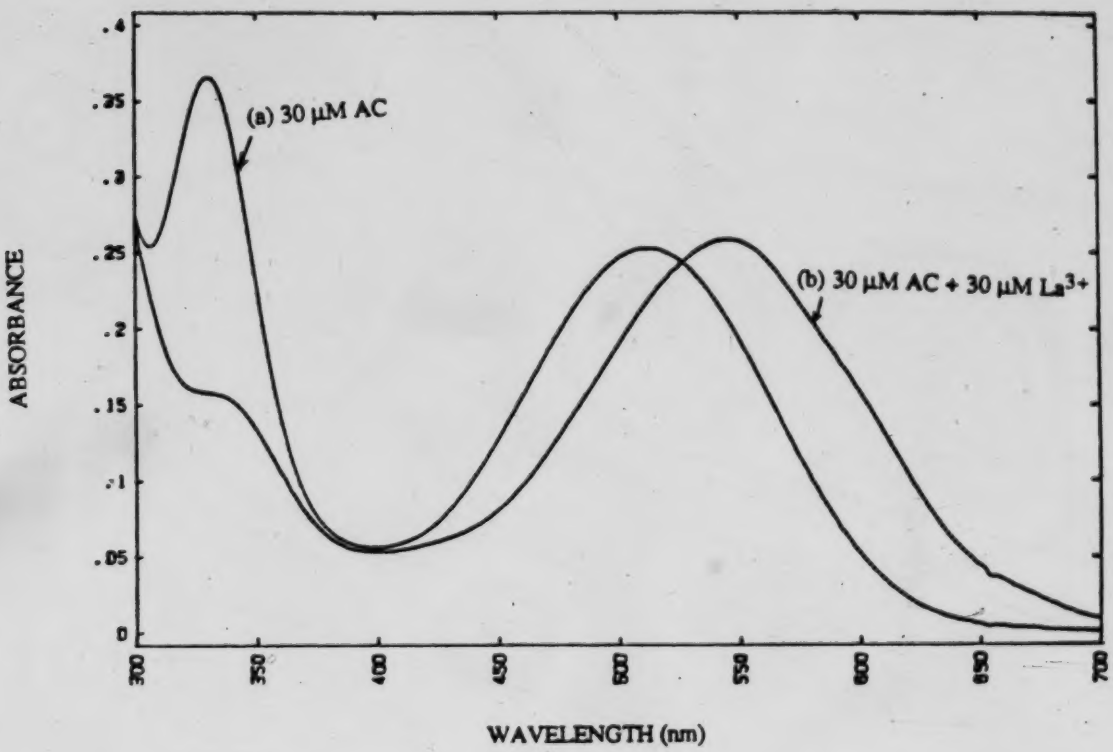
The cyclic voltammetric curves in Figure (3-1) demonstrate that formation of the La•AC complex in solution with a 2:1 La^{3+} to AC ratio results in a new species with a peak reduction potential, E_{pr}, of -0.88 V *vs* SCE, a change of -165 mV at a C electrode, similar to results at Hg. The peak heights are reduced, which can be attributed to the decrease in reversibility of the electrode reaction and also to the diffusion coefficient of the complex being smaller than that of the free ligands. However, this effect was not further explored. Note the complex shows quasi-reversible electrochemical behavior, with a peak separation, ΔE_p, of 150 mV. With ARS as the redox active ligand very similar electrochemical response is obtained; a shift in E_{pr} of -135 mV is observed when 0.2 mM La^{3+} is added to a 0.1 mM ARS, pH 9.2 solution. A 0.1 M NH_4Cl, 0.1 M NH_4OH buffer solution, adjusted to pH 9.2 with HCl, was found to give optimum results for La^{3+} complexation by ARS and AC in solution. This ammonia buffer mixture was used in subsequent measurements unless indicated otherwise.

To examine the question of stoichiometries of La complexes under our solution conditions at pH 9.2, a brief



Figure(3-1). Cyclic voltammetry at a naked glassy C electrode in 0.2 mM Alizarin complexone (AC) (——) and 0.2 mM AC, 0.4 mM La^{3+} (---) in 0.1 M NH_3, 0.1 mM NH_4Cl, pH 9.2 at a scan rate of 100 mV/s.

spectrophotometric study was undertaken. The absorption spectra of AC and La•AC complex are shown in Figure (3-2). Alizarin complexone gives a deep red solution in ammonia buffer at pH 9.2 and shows absorption maxima at 334 and 520 nm, as presented in Table (3-1). When La^{3+} is added to a solution containing AC, the solution turns purple in the time of mixing. The absorption maximum shifts to longer wavelength as $[La^{3+}]$ increases. For a solution containing La^{3+} and AC in a 1:1 ratio, the absorption maximum changes to 553 nm, as evidenced by the absorption spectrum and the data presented in Table (3-1). When $[La^{3+}] > [AC]$, there is very little change in absorption spectra when compared to that of the 1:1 solution. Similar behavior has been observed for [AC] from 500 nM up to 0.2 mM. However, purple precipitates are formed on standing for 4 hours or more when $[La^{3+}]/[AC]>2$ and $[La^{3+}] > 1$ mM. The independence of spectrophotometric behavior on solution concentration suggests that the complexation reactions between La^{3+} and AC remains the same throughout the whole concentration range studied, although this was not examined in detail. The stoichiometries of the $La_x•AC_y$ complexes have been studied by continuous variation methods. A plot of absorbance at a selected wavelength *vs* molar fraction of reactant gives more than one break point, indicating that there is more than one complex formed, and suggesting the formation of La•AC complexes in the ratios of 1:1, 1:2 and even 1:3. However, we do not observe the formation of complexes with stoichiometry in which x > y when



Figure(3-2). Absorption spectra of (a) a 30 µM solution of AC and (b) a solution containing 30 µM AC and 30 µM La^{3+} in ammonia buffer of pH 9.2. Path length = 1cm.

Table (3-1). Values of λ_{max} for Quinone and Quinone•La^{3+} Complexes.

	λ_{max} (nm)	
species	oxidized form	reduced form[b]
AC	334, 520	397, 457
AC•La (1:1)[c]	553	401, 457 (sh)[d]
ARS	334, 520	398, 466
ARS•La (1:1)[c]	536	398, 468 (sh)[d]

a. Wavelength of absorption peak maximum.

b. Reduced form prepared by exhaustive electrolysis of oxidized form in thin layer spectroelectrochemical cell.

c. Complex formed in a solution of 0.2 mM in metal and ligand.

d. This peak for the free ligand becomes a broad shoulder with lower absorptivity (~50%) for the complex.

La^{3+} is in excess. The complex with a 1:1 ratio is probably a 2:2 complex, as suggested by others [4,12].

A detailed study of the 5-sulphonate derivative of alizarin has also been reported at pH 6.2 [11] (note ARS is the 3-sulphonate derivative of alizarin). We undertook a spectrophotometric study of the stoichiometry of La^{3+} and ARS at pH 9.2. Results are very similar to those obtained for the La•AC system. The absorption maximum of the ARS solution shifts to longer wavelength upon complexation with La^{3+}, as presented in Table (3-1). Results obtained from continuous variation methods also suggest the formation of more than one complex. The data are in agreement with those for alizarin 5-sulphonate, in that complexes of both 1:1 and 1:2 metal to ligand ratio are formed. A detailed analysis of the absorbance data such as that done by Deane and Leonard [11] for alizarin 5-sulphonate and La^{3+} was not performed. However, it is reasonable to expect the 1:1 ratio we observe for a La^{3+} and ARS complex in fact corresponds to formation of a 2:2 species, in the same manner as proposed for alizarin 5-sulphonate and La^{3+} [11]. For the latter ligand the extent of formation of the (alizarin 5-sulphonate•La)$_2$ complex is very nearly constant as the ratio of La^{3+} to the ligand increases above 1 [11], and there is no evidence to the contrary for the ARS and La^{3+} complex. We assumed that the La•ARS and La•AC complexes with metal to ligand ratio of 1 are 2:2

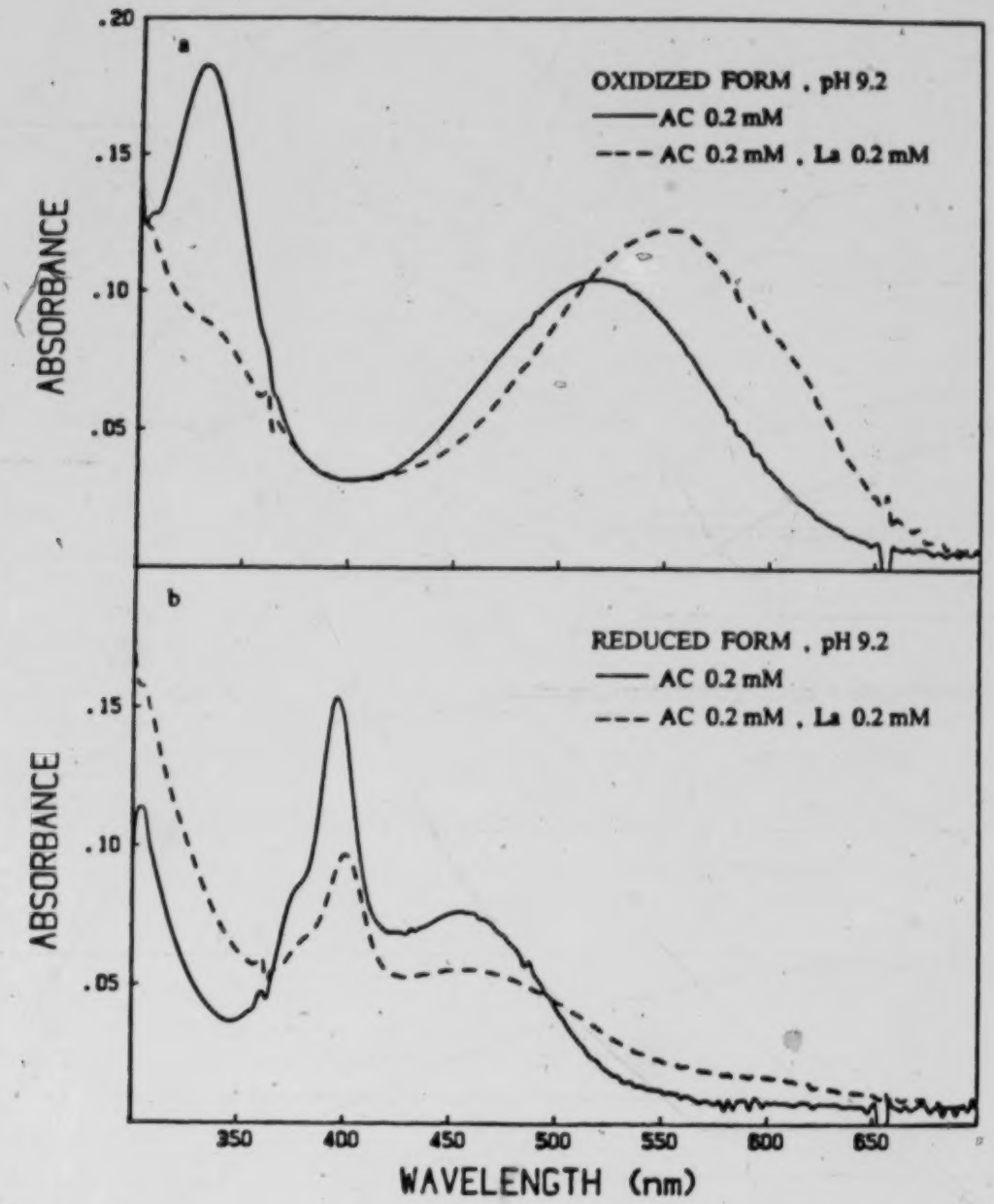
complexes with similar structures as proposed by Deane and Leonard [11].

The pH dependence of 1:1 (or 2:2) complex formation was examined in the presence of excess La^{3+} at a C electrode. At pH 4 in acetate buffer there is no observable shift in E_{pr} for ARS with a twofold excess of La^{3+} present, and no color change is observed on addition of a twofold excess of La^{3+} to an ARS solution. With a five fold excess of La^{3+} a color change and a shift in E_{pr} of -140 mV is observed, although the reaction is not complete and a reduction peak of approximately equal magnitude is observed for the free ligand at -0.42 V. These results are in agreement with spectroscopic data on alizarin 5-sulphonate complexation with La^{3+} showing that no reaction occurs until the pH is increased to a value of 4 to 5 [11]. With AC the equilibrium still weakly favors La•AC complex formation at pH 4 (acetate buffer) as evidenced by the color change when a twofold excess of La^{3+} is added to a 0.1 mM AC solution. The mixture shows two reduction peaks of nearly equal magnitude at -0.465 V corresponding to free ligand, and -0.630 V for the complex. Spectroscopic data for the alizarin complexone 5-sulphonate•La^{3+} complex is very similar, showing complexation begins to occur at pH values of 3 or more [11]. At a pH of 2 or less there is no spectroscopic or electrochemical evidence for formation of either La•AC or La•ARS complexes, in agreement with previous reports for the 5-sulphonate quinone derivatives [11]. Consequently, La^{3+}

complexation by AC or ARS in a polymer coated electrode (*vide infra*) at pH 9.2 can be completely reversed by transferring the electrode to a pH 2 solution, as presented in Chapter 4.

The extent of ionization of the quinone-La^{3+} complexes, and the number of protons involved in equation (3.1), has not been reported due in part to the complicated equilibria involved. We found dichloromethane, benzene, or diethylether extract less than 0.5% of any AC and ARS complexes of La^{3+} formed in aqueous pH 9.2 solutions with a 1:1 metal to ligand ratio, suggesting the complexes are charged. The fact the complexes can be extracted into the quaternized polyvinylpyridine films as discussed in Chapter 4 is consistent with anionic species formation.

Both spectroelectrochemical and electrochemical measurements were undertaken to evaluate the stoichiometry of the reduced La^{3+} complex. Spectroscopic studies of the reduced forms of the free ligands and complexes were obtained with a thin layer spectroelectrochemical cell with an optically transparent electrode. The spectrum of both free AC at 0.2 mM in pH 9.2 buffer, and the complex formed in a 0.2 mM AC, 0.2 mM La^{3+} mixture at pH 9.2 is shown in Figure (3-3a). The respective solutions were then exhaustively electrolyzed to generate the hydroquinone form of AC. Comparison of the two spectra in Figure (3-3b), and the data in Table (3-1), indicates that a complex with different spectral properties from the free hydroquinone persists upon



Figure(3-3). a) Spectra of the quinone form of alizarin complexone (AC) and the La^{3+} complex in a thin layer spectroelectrochemical cell.

b) Spectra of the hydroquinone form of AC and the La^{3+} complex following exhaustive electrolysis at a Hg coated Pt mesh in the spectroelectrochemical cell.

reduction of the AC, La^{3+} mixture. The spectra for the La•ARS complex in oxidized and reduced form were obtained in similar fashion, and indicate a complex is also formed between the hydroquinone form of ARS and La^{3+}, Table (3-1). While the peaks do not shift for the hydroquinone form of ARS in the presence of La^{3+}, the absorptivity at 398 nm decreases ~50% and the shoulder at 468 nm becomes broader and about 40% less intense, extending to longer wavelengths as is the case for AC•La in the reduced form, Figure (3-3b).

An electrochemical study of the dependence of E, determined from the peak potential of a differential pulse voltammogram, on the concentration of La^{3+} was also performed. With a constant concentration for both AC and ARS of 20 μM, $E_{1/2}$ was found to be constant within 2 mV over a La^{3+} concentration range of 30 to 100 μM. Under these conditions, where the 1:1 complex is dominant for the oxidized form, equation (3.5) can be applied. The meaning of $\Delta E_{1/2}$ is more complex if the electron transfer is quasireversible and the prelog term may differ from the Nernstian value [27]. Despite this consideration, lack of a change in $\Delta E_{1/2}$ for the complex, when combined with the spectral data, provides evidence that the stoichiometry remains unchanged for both oxidized and reduced species in the presence of excess La^{3+} [25].

3.4 Conclusion

La^{3+} forms stable complexes with alizarin derivatives (ARS and AC) in ammonia buffer at pH 9.2, while the equilibrium shifts to free ligand formation at pH values lower than 4. Complexes with a 1:1 metal to ligand ratio predominant when $[La^{3+}] \geq [Q]$. This 1:1 complex is expected to have a stoichiometry of 2:2, on the basis of previously published work. Spectroelectrochemical studies show that the stoichiometry remains unchanged when the complex is reduced. In addition, the half-wave potential of the complex is found to be independent of $[La^{3+}]$ at constant quinone concentrations. The change in $E_{1/2}$ of the free ligand upon complexation is then only a function of the metal ion. As a result, the change in $E_{1/2}$ can be used to identify the metal ions involved in complexation with the alizarin derivatives.

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Chapter 4 Mass Transport Effects in Electroanalysis of La^{3+} with Alizarin Derivatives at Quaternized Polyvinylpyridine Modified Electrodes

4.1 Introduction

Chemically modified electrodes (CME) have been the subject of intense research for a number of years [1-5]. The nature of physical phenomena governing CME behavior has been examined in detail and many characteristics are now well understood. However, while several papers have appeared [6-16], exploration of the analytical utility of redox and ionic polymer modified electrodes has been relatively limited. A comprehensive understanding of factors that govern the performance of polymer modified electrodes as analytical tools, such as the properties of the polymer matrices, is still emerging [16-18]. In many cases [8,10,11] the coulombic interactions within the polymer do not alone provide sufficient insight into the differing substrate transport behavior of the systems.

The large number of analytical complexation reactions developed for which one, or several, of the species involved is electroactive makes the development of ligand complexation

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based modified electrodes very attractive [6,8,10]. An experimental understanding of the factors that influence electrode performance will be important in utilizing the range of ligands available. These include the reversibility of the analytical reaction within an electrode film [6,9,10,18], and the effect of the polymer matrix on complexation [18] and mass and electron transfer processes [4,5,17] within the polymer. Equally important is an understanding of the influence of polymer charge and functionality, in terms of coulombic and permselectivity effects, on the overall extraction process of an analyte into an electrode film.

As part of a study of the effects of ligand properties, polymer charge, and film thickness on analytical complexation reactions at CME's we have examined the electrochemically reversible anthraquinone derivatives alizarin red S (ARS) and alizarin complexone (AC), ion exchanged into partially quaternized polyvinylpyridine (QPVP) films on carbon electrodes, C/$[QPVP]_{surf}$. The alizarin derivatives have rich analytical metal complexation chemistry, and have been used in solution to electrochemically determine electroinactive metals [19-23], and as colorimetric reagents for a number of metal species [24-28]. It is known that protonated polyvinylpyridine (PVP) is relatively permselective [3], at least partially excluding many cations from the polymer bulk, and cationic QPVP has similar properties [8,17,29]. The

ability of an additional ligand incorporated in the polymer film, with a strong affinity for the metal ion, to overcome exclusion of the ion by the polymer matrix can thus be readily examined using QPVP. The influence of the matrix is a question of fundamental interest in the design of analytically useful modified electrodes, and the important role of film thickness on electrode performance in such a situation is illustrated in this paper. In addition it is found that a change in film transport properties can be used as a source of analytical information.

4.2 Experimental

Poly(4-vinylpyridine) (PVP) (MW 500,000) was a kind gift from Reilly Tar and Chemicals Corp. Quaternized PVP was obtained by reaction of benzyl chloride with 2 gm of PVP in 100 ml of refluxing methanol (22 h) [29]. After solvent evaporation, a crude product was obtained and then was redissolved in a minimum amount of methanol. This methanol solution was precipitated in diethylether and the precipitate was filtered and dried under vacuum overnight. A white powder was obtained. Extent of quaternization, controlled by the molar ratio of benzyl chloride to pyridine moieties in PVP (0.66) used, was determined to be 64% by elemental analysis. (Found: molar ratio Cl/N = 0.64, Cl 12.12%, N 7.45%, C 66.05%, H 5.84%; Calc.: Cl 12.20%, N 7.53%).

Alizarin red S and alizarin complexone were used as received (Aldrich). Water was doubly distilled from alkaline permanganate. All other chemicals were reagent grade.

Cyclic voltammetry and rotating disc voltammetry were performed with a Pine Instruments RDE-4 Potentiostat, Pine MSR Rotator, and a Kipp and Zonen BD90 X-Y recorder. A PAR 174A Polarographic Analyzer and Houston Instruments X-Y recorder were used for differential pulse (DP) voltammetry, with a scan rate of 1 mV/s, modulation amplitude of 5 mV and 0.5 s drop time. Chronoamperometry was performed with a PAR 273 with an IBM-PC-XT interfaced as controller and data acquisition system.

Glassy carbon rods (Atomergic Chemetals, N.Y.) were sealed in teflon sleeves, polished with alumina (Beuhler) to a 1 μm final polish, and rinsed in an ultrasonic bath. Pt flag electrodes for Auger electron analysis were contacted with Cu leads, and sealed in epoxy (Hysol-Clear) to leave one exposed face. A stock 2 mM QPVP (expressed as moles of vinylpyridine monomer), 0.05 mM α,α'-dibromo-p-xylene methanol solution was prepared, and dilution of this to give 25 μM QPVP was necessary to obtain thin polymer films. In a closed container, saturated in methanol vapor, a few drops of polymer solution were slowly evaporated (~ 3 h) on an electrode surface and then baked at ~ 60°C for 4 h in air. Evaporation in a methanol atmosphere produced more uniform films. Addition of α,α'-dibromo-p-xylene and baking at 60°C

gave much more durable QPVP films, as previously reported [17].

To determine polymer coverage an electrode was soaked 5 min in 1 mM $K_4Fe(CN)_6$ or $K_3Fe(CN)_6$ (0.1 M trifluoroacetate, pH 2), rinsed, transferred to pH 2 blank solution, and a cyclic voltammogram recorded at 10 or 20 mV/s. The total polymer coverage, expressed in pyridine units, Γ_{py}, was calculated assuming total charge compensation by the redox species [30]. At pH 2 any remaining tertiary pyridine is protonated so the total number of pyridine sites can be determined. $Fe(CN)_6^{3-}$ is recognized as a strong acid while $Fe(CN)_6^{4-}$ will exist as $H_2Fe(CN)_6^{2-}$ at pH 2 [31]. This point was not recognized in most of the work in this thesis and Γ_{py} was calculated assuming the $Fe(CN)_6^{4-}$ species was present at pH 2. Comparsion of results for Γ_{py} measured using $Fe(CN)_6^{3-}$ then $Fe(CN)_6^{4-}$ (after first exchanging out the other ion in 4M KCl) at pH 2 and assuming charges of 3^- and 4^- respectively showed a discrepancy in Γ_{py}. The value of Γ_{py} was 31.6% ± 15.4% greater for $Fe(CN)_6^{4-}$. In fact this result is consistent with predominately $HFe(CN)_6^{3-}$ in the film at pH 2. On the other hand, when Γ_{py} was determined at pH 2 and 7 using $Fe(CN)_6^{4-}$ only 1 to 5 % discrepancies were measured, as was also the case when working with $Fe(CN)_6^{3-}$. This result suggests there is no change in the charge state for $Fe(CN)_6^{4-}$ between pH 2 and 7 in the polymer. Further, for an electrode with a known weight of QPVP deposited on a portion of the

surface, Γ_{py} determined by $Fe(CN)_6^{4-}$ exchange at pH 2 was within 85 to 95% of the expected value based on the weight of deposited polymer. This indicates that mostly $Fe(CN)_6^{4-}$ exists in the film at pH 2. Given the uncertainty in the measurements and the discrepancies outlined above it was decided to use the Γ_{py} value determined by $\Gamma_{Fe(CN)_6^{4-}}$ as a measure of polymer thickness. As well the bulk of the data had been obtained in this manner, so it was decided to continue in this way for the sake of comparison. Given that the polymer thickness may be over-estimated by a factor of 1.3 ± 0.15, the absolute value of D_{ct} may be over-estimated by a factor of 1.7. However, the precision of D_{ct} in comparing results for different electrodes is independent of this question of accuracy. Finally, the agreement of Γ_{py} at pH 7 and pH 2 for the strong acid $Fe(CN)_6^{3-}$ indicates nearly complete quaternization of the QPVP occurs due to the presence of cross-linking agents. The thickness of the polymer film was calculated from $d = \Gamma_{py}/\rho_{py}$, where ρ_{py} is the molar density of pyridine moieties in the dry film and $\rho_{py} = 2.4$ mmole/cm^3 as presented in Table (5-1), details of density measurements are shown in Chapter 5.

Distribution coefficients, K_D, taken as the ratio of concentration of redox ion in the QPVP film to solution concentration, were determined following the method of Szentirmay and Martin [32]. A 0.1 M ammonia buffer of pH 9.2 was used as supporting electrolyte. At concentrations less

than 1 μM electrodes were allowed to equilibrate in stirred solution for 24 to 30 h, which was sufficient time to reach a nearly constant film concentration. At low concentrations the QPVP film was sometimes partially lost from the electrode, and results were discarded when this occurred. At concentrations greater than 1 μM equilibration times of 1 to 4 h proved sufficient.

The diffusion coefficient for charge transfer was usually determined by chronoamperometry using the Cottrell equation $i = nFA\ D_{ct}^{1/2}\ \Gamma_{Redox}/d(\pi t)^{1/2}$, where n, F, A, and t have their usual meanings, Γ_{Redox} is the coverage of redox species in mol/cm^2 and d is polymer thickness. A potential step was performed in a solution of supporting electrolyte (0.1 M ammonia buffer) to determine the charging current, before ion exchanging the redox ion into the film from a 1 mM solution. This current was then subtracted from the current observed with redox ion present in the film, giving linear Cottrell plots at shorter times, with an intercept of zero. Coverage of redox ion, Γ_{Redox}, was measured by cyclic voltammetry (10 mV/s) immediately following the potential step. For some electrodes D_{ct} was also evaluated by rotating disk voltammetry to determine the charge transfer limited current by a steady state method; thick films were used to ensure charge transport was the rate limiting step. This condition was confirmed as described previously [30] by the independence of limiting current on solution concentration of

the redox couple, and the agreement between D_{ct} determined by rotating disk voltammetry and chronoamperometry.

Permeability [33-35] of Eu^{3+} through QPVP films was measured by rotating disk voltammetry in a solution containing 1 mM Eu^{3+}, 0.5 mM 1,5-naphthalenedisulphonate and 0.1 M KCl in 0.1 M acetate buffer at pH 5.5. Naphthalenedisulphonate was ion-exchanged into the polymer film to resemble the structural environment when the alizarin derivatives were extracted into the film. In addition, naphthalenedisulphonate is electroinactive over the potential range examined so it did not interfere with the electrochemistry of Eu^{3+}. The potential was stepped to - 1.3 V *vs* SCE and the current was measured as a function of rotation rate, ω. Since there is no electron transfer agent bound in the polymer film, the current measured must result from Eu^{3+} ions that permeate through the film to the electrode surface. By plotting $1/i$ *vs* $1/\omega^{1/2}$, a straight line with nonzero intercept was obtained. The film current term in equation 1.3 is then equal to the substrate diffusion current, i_S, as discussed in Section 1.4. The current is given by $nFAK_DD_PC_A/d$ [33], where n, F and A have their usual meanings, d is the polymer thickness, C_A is the bulk concentration of redox species, K_D is the distribution coefficient and D_P is the diffusion coefficient in the polymer. The intercept of the $1/i$ *vs* $1/\omega^{1/2}$ plot , $1/i_S$, equals $d/nFAK_DD_PC_A$. The slope is given by the inverse of the

Levich equation slope and equals $1/(0.62nFAD^{2/3}\nu^{-1/6}C_K^*)$, where D is the solution diffusion coefficient and ν is the kinematic viscosity of the solution. The slope of the inverse Levich plot is then a function of the solution diffusion coefficient of Eu^{3+}, as also shown explicitly in equation 1.3. An apparent permeability, $K_D D_P$, was obtained from the intercept of the inverse Levich plot [34-35]. Since Eu^{3+} is very similar to La^{3+}, the apparent permeability of $Eu^{3+/2+}$ ions can then be used as an estimate of that for La^{3+} through the QPVP films.

A Physical Electronics Scanning Auger Spectrometer, model 595 (Surface Analytical Laboratory, Dept. of Physics, Simon Fraser University [SFU]) was used for Auger electron survey and depth profile analyses of surface modified Pt electrodes. Samples were prepared and then transported to SFU and examined by D.J.Harrison with the assistance of B.Heinrick of SFU. A 3 keV electron beam, at a current of 50 to 100 nA, served as excitation source. Depth profiles were obtained by sputtering with a 3 keV Ar^+ beam while scanning the element peaks of interest. Energy windows were C (240 to 300 eV), Pt (53 to 69 eV), La (70 to 90 eV and 600 to 647 eV). A Pt substrate was used to allow determination of the polymer/substrate interface during depth profiles.

4.3 Results and Discussion

Polymer Modified Surfaces

The simplest route to preparation of a modified electrode is through ion exchange of anionic ARS or AC into a quaternized polyvinylpyridine film [1-3,8,10,29] on a C electrode surface, to give a quinone modified electrode, $C/[QPVP \cdot ARS]_{surf}$ or $C/[QPVP \cdot AC]_{surf}$. At pH 9.2 more than 98% of ARS is present in the 2^- form [24,36], while based on the pK_a's for AC approximately 80% is present as the dianion and 20% is in the 3^- form [37]. The alizarin derivatives are strongly bound in the polymer film, as determined from the partition isotherm for extraction of electroactive ions over a concentration range of 20 nM to 1 mM. Values of the apparent distribution coefficients, K_D, are reported in Table (4-1). At concentrations of 1 μM or less the isotherm is linear and the values of K_D are on the order of 10^4 to 10^5, while above 0.1 mM the polymer nears saturation and K_D decreases. For $Fe(CN)_6^{3-/4-}$ equilibrium is established and atrue distribution coefficient is measured. However, even after 24 h soaking in 2 M KCl 70-80% of the quinone remains in the film, whereas all of the $Fe(CN)_6^{3-/4-}$ can be removed. Consequently, while the measured distribution coefficients clearly indicate the very strong affinity of $[QPVP]_{surf}$ for the quinones and the 1:1 La:AC complex they may not reflect the true value of K_D. This is shown in Figure

(4-1) by the cyclic voltammetric response of a C/$[QPVP]_{surf}$ electrode in a blank solution, pH 9.2, containing only ammonia buffer, following soaking in a 1 mM $Fe(CN)_6^{3-}$, 1 mM ARS, pH 9.2 solution. The ratio of surface coverages, $\Gamma_{ARS}/\Gamma_{Fe(CN)_6^{3-}}$, for such an experiment is typically 3.5 to 4 despite the fact the distribution coefficients favor $Fe(CN)_6^{3-}$ over ARS by a factor of ~ 2. Apparently the irreversibility of the quinone extraction results in its dominance in the film, demonstrating the poor predictive power of the apparent K_D values. The hydrophobic nature of the quinones, their relatively large size, and the distance of separation of the multiple charge sites on the ions may decrease mobility once bound in the film compared to inorganic complexes and the singly charged quinones previously studied [30].

Several qualitative studies have shown that cations such as $Ru(NH_3)_6^{3+}$ and $Co(bipyridyl)_3^{3+}$ do not easily penetrate $[QPVP]_{surf}$ or protonated $[PVP]_{surf}$ films [3,8,17,29,30], as evidenced by 90 to 99% reduction in cyclic voltammetric peak heights. A knowledge of the permeability or K_D for La^{3+} in $[QPVP]_{surf}$ films would aid in determining whether metal transport or extraction in the film is a limiting process in complex formation. Unfortunately, due to the difficulty in preparing pin-hole free films, attempts to quantitatively determine the permeability of La^{3+} by the method of Anson and co-workers [38] were unsuccessful. The permeability of a

Table (4-1). Distribution Ratio, K_D, in the QPVP Matrix.

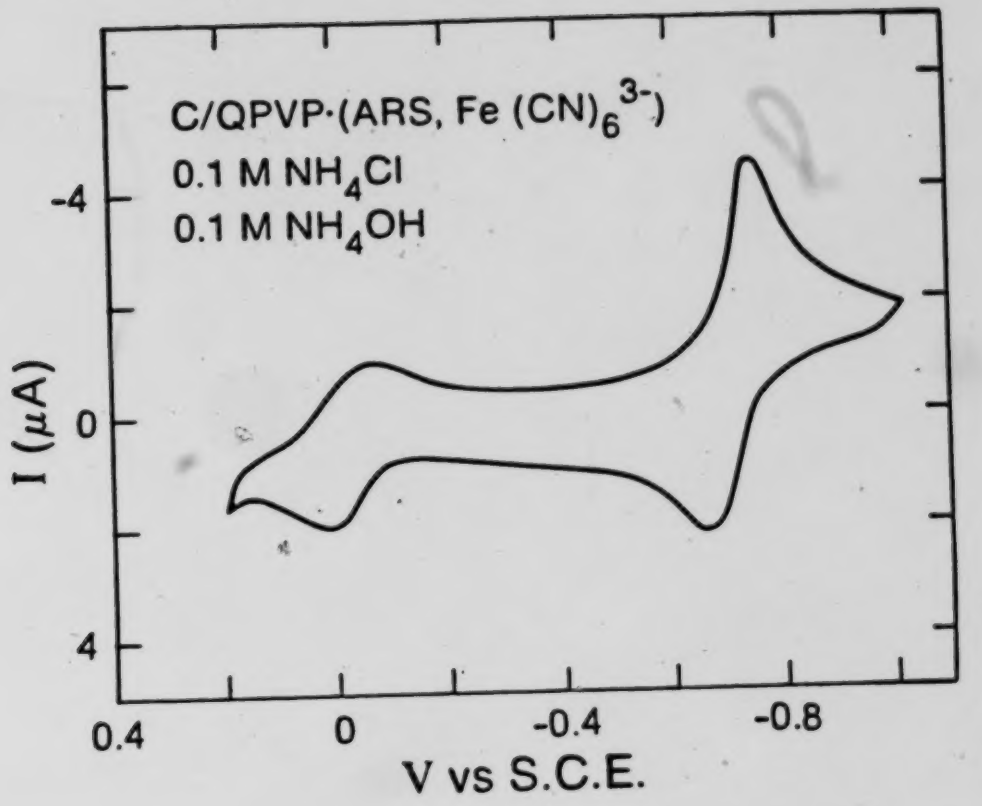
ion	K_D[a] concentration range 0.02-1 μM[b]	1 mM[c]
$Fe(CN)_6^{4-}$	2.7×10^5	411
$Fe(CN)_6^{3-}$		266
ARS^{2-}	1.2×10^4	156
AC^{2-}	2.4×10^4	372
ACLa (1:1)[d]	4.4×10^4	

a. Distribution ratio, $K_D = C_p/C_s$, at pH 9.2, 0.1 M NH_4Cl, 0.1 M NH_4OH supporting electrolyte.

b. Determined from the slope of the linear portion of the partition isotherm over the range 0.02 to 1 μM.

c. Determined at 1 mM.

d. Prepared as a 1 to 1 mixture of AC and La^{3+}.



Figure(4-1). A C/[QPVP•ARS, $Fe(CN)_6^{3-}]_{surf}$ electrode response in pH 9.2 solution of supporting electrolyte alone, following equilibration in a 1 mM ARS, 1 mM $K_3Fe(CN)_6$, pH 9.2 solution. The charge on ARS is 2^- at pH 9.2, and it clearly competes strongly with $Fe(CN)_6^{3-}$ for ion exchange sites in the polymer.

similar but electroactive ion, $Eu^{3+/2+}$, was examined by rotating disk voltammetry at a $C/[QPVP]_{surf}$ electrode. Detailed experimental procedures to determine the permeability have been presented in Section 4.2. A permeability, $K_D D_P$, where K_D is the distribution coefficient and D_P is the diffusion coefficient in the polymer, of ~ 3 x 10^{-8} cm^2/s, was measured for 1 mM Eu^{3+} from the intercept of the inverse Levich plots assuming the current was limited by permeation of redox species through the polymer [34-35]. However, the slopes of the inverse plots gave a value for the solution diffusion coefficient of Eu^{3+} 10 to 100 times smaller than the value measured at a naked carbon electrode. The most likely explanation for this is the presence of pinholes in the polymer surface coating that serve as the primary path for transport of Eu^{3+} to the electrode. The surface area term in the Levich equation would then be reduced to the area of the pinholes, accounting for the small apparent values for Eu^{3+} diffusion in solution. The observed permeability is then an upper limit for permeation of metal ion through the polymer bulk, which could in fact be much lower. This interpretation is consistent with the Auger depth profile data presented below.

Large quantities of ARS or AC can be electrochemically accessed within the films, but when Γ_{py} ~ 10^{-8} mol/cm^2 only 40 to 80% of the quinone present is electroactive. This was determined by comparing the apparent Γ_{py} coverage determined

by sequentially exchanging $Fe(CN)_6^{4-}$ and either ARS or AC into the polymer films from 5 mM solutions, and recognizing that $\Gamma_{Fe(CN)_6^{4-}}$ is a relatively reliable indicator of the total pyridinium sites present [30]. When $\Gamma_{py} < 10^{-8}$ mol/cm^2 the films can be totally charge compensated by the alizarin derivatives based on the electrochemistry, which indicates that all of the quinone present is electroactive.

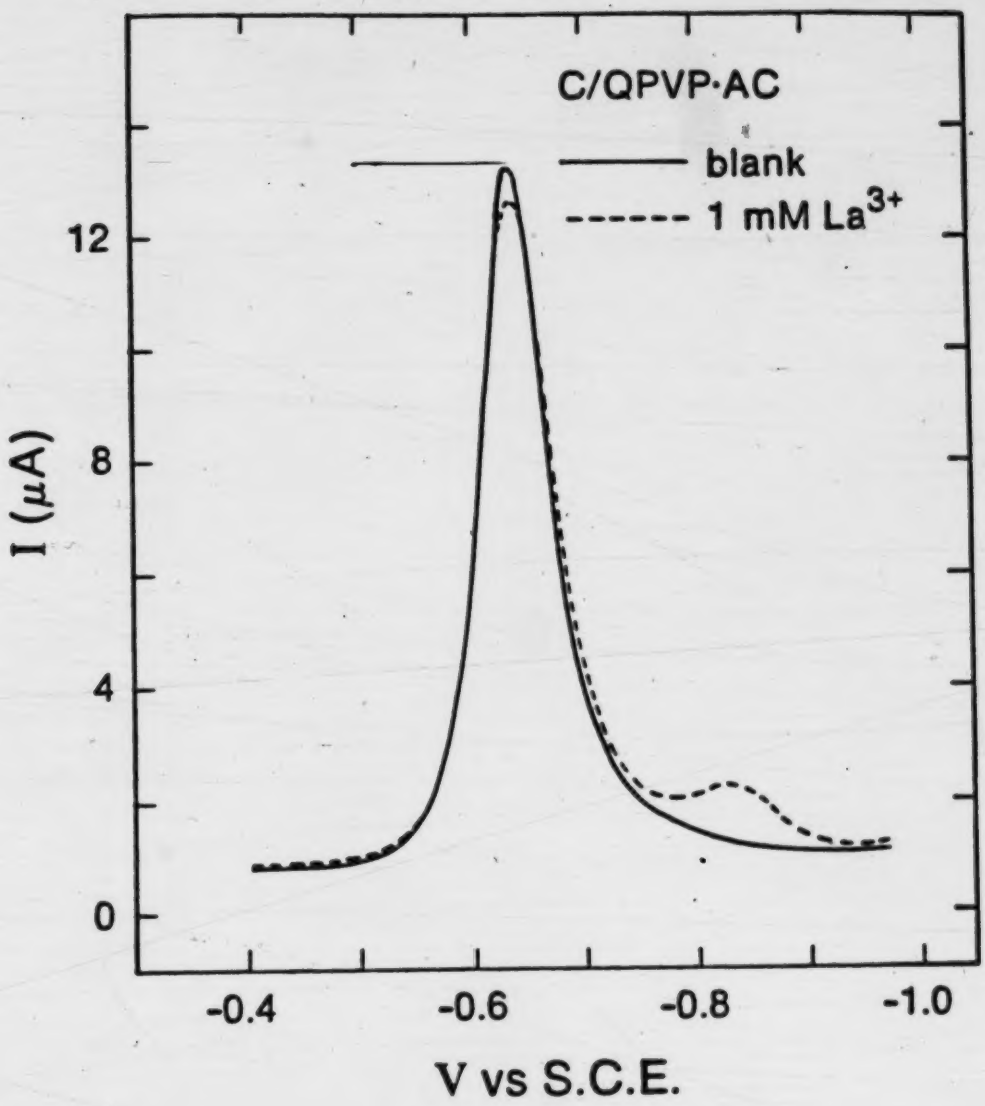
The apparent diffusion coefficient for charge transport, D_{ct}, by ARS or AC in the QPVP film has been determined by chronoamperometry in solutions of supporting electrolyte, pH 9.2, and by rotating disc voltammetry [2,3-5,30], in 5 mM quinone, pH 9.2. The results indicate a slow charge transport process, with D_{ct} varying from 0.2 to 1 x 10^{-10}cm^2/s for both free ligands in relatively thick polymer films (Γ_{py} = 10^{-8} to 10^{-7} mol/cm^2). In comparison D_{ct} for oxidation of $Fe(CN)_6^{4-}$ at pH 9.2 in the same polymer is 1 to 3 x 10^{-10} cm^2/s. The absolute magnitude of D_{ct} is subject to some uncertainty as discussed in Section 4.2.

Thick Film Behavior

Initial experimentation with relatively high coverage of polymer films, 5 x 10^{-9} to 5 x 10^{-8} mol/cm^2 of pyridine sites, demonstrated that a $La_x \cdot AC_y$ complex is formed within the $[QPVP \cdot AC]_{surf}$ film. A differential pulse (DP) voltammogram of a C/$[QPVP \cdot AC]_{surf}$ electrode in a blank, pH 9.2 solution

results in a peak at -0.64 V for the surface bound quinone, Figure (4-2). Transfer to a 1 mM La^{3+} solution, pH 9.2, gives a differential pulse voltammogram with a peak at -0.64 V for AC, and a new peak at ~ -0.82 V as shown in Figure (4-2). Similarly a $C/[QPVP \cdot ARS]_{surf}$ electrode develops a new peak at ~ -0.81 V on exposure to La^{3+}, with the same ratio of free ligand to complex peak current as observed for AC modified electrodes. These results are consistent with partial conversion of the quinone, Q, in the film to a $La_x \cdot Q_y$ complex, although the stoichiometry of the complex is undetermined. The extent of complex formation appears small, and the peak current for the complex is relatively independent of La^{3+} concentration, showing a high degree of scatter in i_p as La^{3+} concentration is varied from 0.05 to 2 mM. Given the difficulty with pinhole formation in the film the current for the complex may arise from complex formed near the electrode surface in the vicinity of a pinhole. This would account for the variability observed.

In contrast, if a $C/[QPVP]_{surf}$ electrode is exposed to a 0.2 mM AC, 0.2 mM La^{3+}, pH 9.2 solution, in which a 1:1 complex already exists, then a DP voltammogram shows a single peak at -0.83 V. Exposure of a $C/[QPVP \cdot AC]_{surf}$ electrode to the same solution does not result in significant formation of the complex in the film. These results indicate that the complex is durable within the film, and can diffuse into an electrode which initially contains no strongly bound species



Figure(4-2). Differential pulse voltammogram of high coverage, Γ_{py} = 2 x 10^{-8} mol/cm^2, C/$[QPVP{\cdot}AC]_{surf}$ electrode in blank, pH 9.2 supporting electrolyte (——) and with 1 mM La^{3+} added (---). Scan rate 1 mV/s,modulation amplitude 5 mV, drop time 0.5 s.

such as AC or ARS. However, the complex is apparently unable to diffuse rapidly in a film which is pre-saturated in quinone. This may reflect a change in film structure when the bulky quinone acts as counterion, a well documented occurrence [1-5,29] for more highly charged ions such as $Fe(CN)_6^{3-/4-}$ in polycationic films.

An Auger electron depth profile of a thick film $Pt/[QPVP \cdot ARS]_{surf}$ electrode, $\Gamma_{py} = 6.5 \times 10^{-8}$ mol/cm^2, exposed to 1 mM La^{3+}, pH 9.2, is shown in Figure (4-3a). The depth profile reveals that La is present primarily at the solution/polymer interface and does not permeate the entire film. Depth profiling of $Pt/[QPVP \cdot AC]_{surf}$ electrodes prepared in the same manner also show this phenomenon. Depth profiles of $Pt/[QPVP]_{surf}$ electrodes exposed to 1 mM La^{3+}, pH 9.2, with no quinone present show that La^{3+} does not penetrate the $[QPVP]_{surf}$ film. In some cases a small La signal is observed on an initial survey scan, but the signal is ~ 30 times smaller than that for $Pt/[QPVP \cdot ARS]_{surf}$ electrodes exposed to La^{3+} at pH 9.2, and is not present after even a brief Ar^+ sputter (~ 5 s). A $Pt/[QPVP]_{surf}$ electrode exposed to a 0.1 mM ARS, 0.1 mM La^{3+}, pH 9.2 solution was also examined and the depth profile indicated a uniform La^{3+} distribution up to the polymer/electrode interface. This confirms the conclusion, based on electrochemical measurements (*vide supra*), that the complex is readily transported in a fresh $[QPVP]_{surf}$ film containing no quinone. For modified

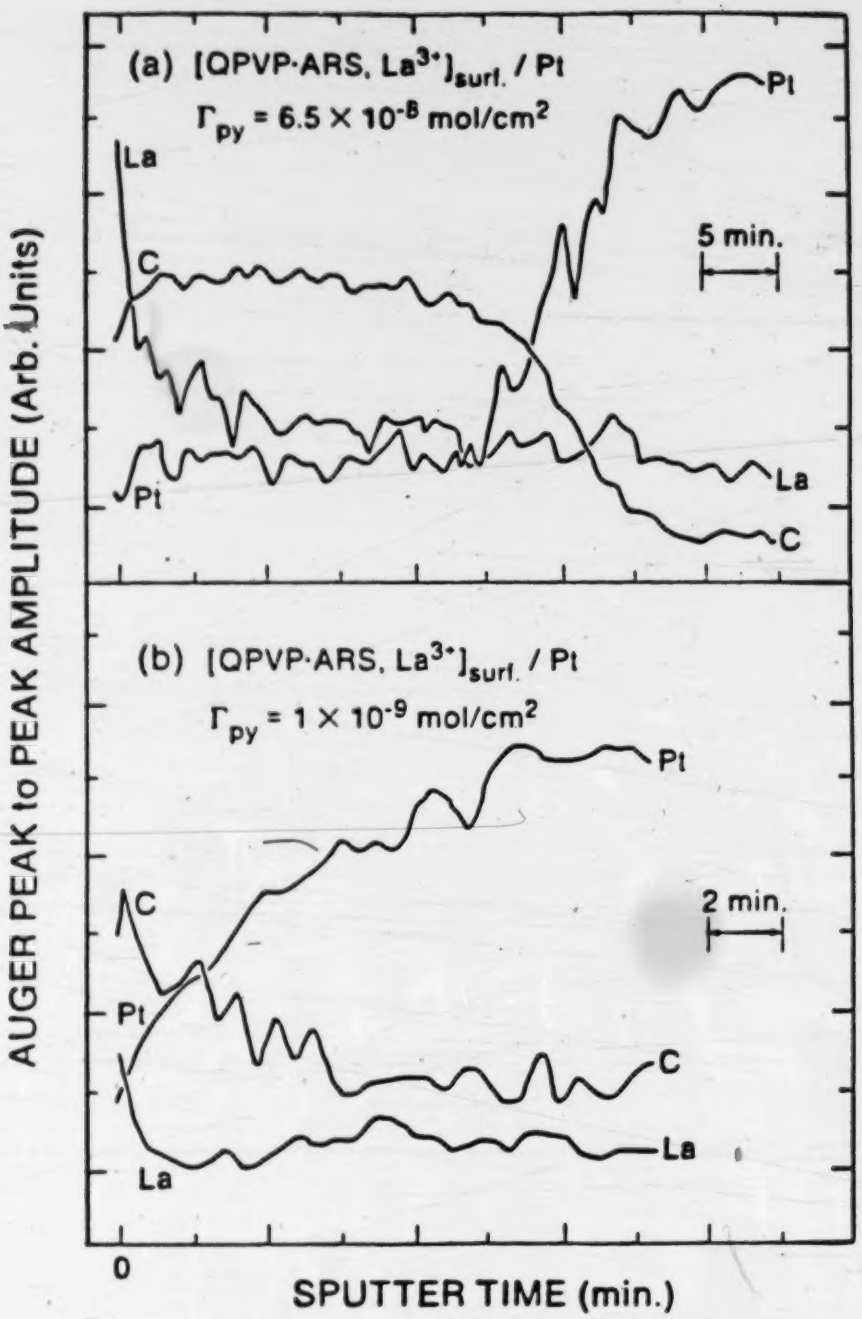


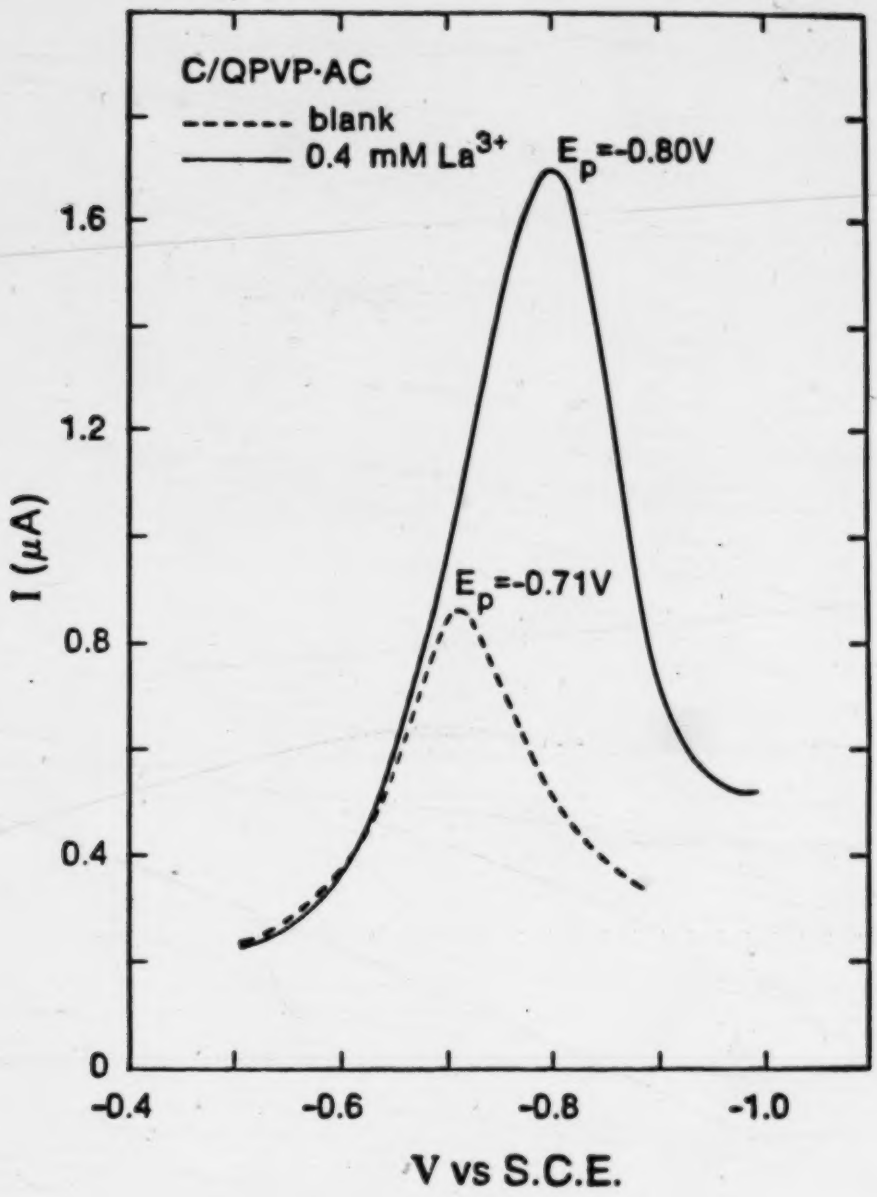
Figure (4-3). Auger electron depth profile of (a) high coverage Pt/[QPVP•ARS]$_{surf}$ electrode, Γ_{py} = 6.5 x 10-8 mol/cm^2, and (b) low coverage Pt/[QPVP•ARS]$_{surf}$ electrode, Γ_{py} = 1 x 10^{-9} mol/cm^2, after exposure to 1 mM La^{3+}, pH 9.2 solution.

electrodes sequentially exposed to ARS or AC, then La^{3+} solutions, depth profiling demonstrates that La^{3+} transport is a serious problem within [QPVP•ARS or AC]$_{surf}$ films, despite the ability of the quinone containing films to extract La^{3+} from solution.

Thin Film Behavior

To offset the problem of low La^{3+} transport rates, much thinner QPVP films have been used, with $\Gamma_{py} \sim 2 \times 10^{-9}$mol/cm^2. Figure (4-3b) shows a depth profile of a Pt/[QPVP•ARS]$_{surf}$ electrode, $\Gamma_{py} = 10^{-9}$ mol/cm^2, that was exposed to a 1 mM La^{3+}, pH 9.2 solution. The Pt signal is observed in an initial survey scan, indicating film thickness of less than 30 Å or the presence of pinholes in the film. This is consistent with the measured Γ_{py} value for which a thickness of ~ 30 Å is expected; additionally the uniformity of such a thin film is uncertain. Significantly, the La signal declines at nearly the same rate as that for C, indicating La is present throughout the film. The electrochemical response (*vide infra*) is also consistent with nearly complete permeation of La^{3+} within thin [QPVP•ARS]$_{surf}$ films.

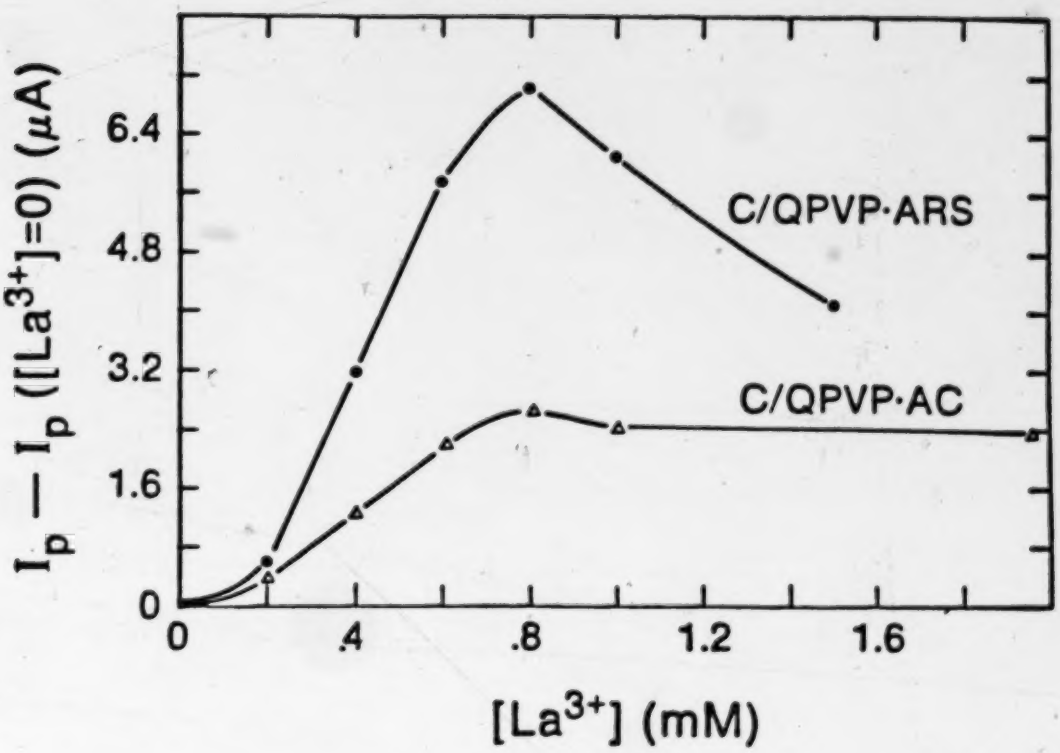
A DP voltammogram in a blank, pH 9.2 solution of a thin film C/[QPVP•AC]$_{surf}$ electrode with $\Gamma_{py} = 2.0 \times 10^{-9}$ mol/cm^2 shows a reduction peak at -0.71 V *vs* SCE, Figure (4-4). This is equal to E_{pr} for the solution species and is ~ 60 mV more negative than for AC in thicker films. The difference in



Figure(4-4). Differential pulse voltammogram of C/[QPVP•AC]$_{surf}$ electrode, Γ_{py} = 2 x 10^{-9} mol/cm^2, in blank, pH 9.2 supporting electrolyte (---), and after transfer to a 0.4 mM La^{3+}, pH 9.2 solution (——). See text for a discussion of electrode preparation.

potentials suggests the environment in the thin polymer film differs from that of the bulk polymer and is perhaps more "water-like" or open in structure. However, the thickness dependence of the potential shift was not examined further. The most striking effect upon immersion of the electrode in La^{3+} solution is the large increase in peak height, which is accompanied by a voltage shift of E_{pr} to -0.80 V in 0.4 mM La^{3+}, pH 9.2. We find that the change in i_p for a C/[QPVP•AC or ARS]$_{surf}$ immersed in La^{3+}, pH 9.2 solution is proportional to La^{3+} concentration over a limited range. A plot of the increase in i_p, determined as i_p for the quinone in a La^{3+} containing solution minus the peak current in a blank solution, $i_p - i_p([La^{3+}]=0)$, is shown in Figure (4-5) for both quinone ligands. Between exposure to La^{3+} solutions, the concentration of quinone in the polymer is recovered by immersion in a 5 mM solution of ARS or AC. Repeated transfers between a quinone solution and a solution of a given La^{3+} concentration do not result in further change in i_p in the La^{3+} solution. Consequently, the increase in i_p with increasing $[La^{3+}]$ cannot result from an increase in complexing agent within the polymer film during re-exposure to quinone solutions.

Using chronoamperometry the diffusion coefficient for charge transfer in the [QPVP•AC, La^{3+}]$_{surf}$ film was determined as a function of $[La^{3+}]$ in solution. The term $CD^{1/2}$, where C is the concentration of the ligand in the film, increases



Figure(4-5). Dependence of net peak reduction current, expressed as $i_p - i_p([La^{3+}]=0)$, on La^{3+} concentration determined by differential pulse voltammetry at pH 9.2 for (●) $C/[QPVP \cdot ARS]_{surf}$ electrode with $\Gamma_{py} = 1.2 \times 10^{-9}$ mol/cm^2 and for (▲) $C/[QPVP \cdot AC]_{surf}$ electrode with $\Gamma_{py} = 2 \times 10^{-9}$ mol/cm^2. Solid lines are for clarity only, to connect data points.

~ 50% as the La^{3+} solution concentration increases up to 0.8 mM, and then decreases at higher concentrations. This data is consistent with the observed changes in differential pulse peak height [39] at the modified electrode. The cause of the effect is uncertain, but, since it does not arise from an increase in complexing agent in the film, it is most likely due to changes in film crosslinking and structure as the $La_x \cdot AC_y$ complex is formed. Increases in D_{ct} as the extent of ionic crosslinking decreases are a common observation for electrostatically bound redox species. Since the anionic charge of the quinone•La complex will be lower than that of the free quinone, ionic cross-linking would be expected to decrease as more La^{3+} is extracted into the film.

The decline in signal observed at high $[La^{3+}]$ at the modified electrode is consistent with a decline in i_p observed at naked electrodes in 0.2 mM ARS solution when $[La^{3+}]$ is greater than 1 mM. This may be due to the complex series of hydrolysis equilibria for La^{3+} at high pH that includes formation of polynuclear La species [36] as the La^{3+} concentration increases. Additionally, in solutions with $[La^{3+}] > 1$ mM and $[La^{3+}]/[Q] > 2$ we observe formation of a purple precipitate upon standing for 24 h.

The shift in peak potential caused by exposure of $C/[QPVP \cdot ARS \text{ or } AC]_{surf}$ electrodes to La^{3+} is irreversible at pH 9.2. Exposure to a pH 9.2 solution with no La^{3+} present,

with or without the quinone in solution, does not result in loss of La^{3+} from the film and return to the peak potential of the free quinone. However, as discussed earlier in Chapter 3 of the thesis, the conditional equilibrium constant does not favor complex formation in solution at pH 2 (CF_3COOH buffer), and exposure of a C/[QPVP•ARS or AC, $La^{3+}]_{surf}$ electrode to a pH 2 solution could be expected to result in dissociation of the complex in the film. In fact, following 5 min of soaking of a C/[QPVP•ARS or AC, $La^{3+}]_{surf}$ electrode at pH 2, subsequent return to a pH 9.2 solution containing no La^{3+} or quinone shows the quinone remains in the film but the La^{3+} is removed. This is evidenced by a shift in E_{pr} back to the original peak potential prior to La^{3+} exposure. Returning this electrode to a solution containing La^{3+} at pH 9.2 gives a peak current within 5% of the value obtained in the first exposure to La^{3+}. This effect allows the same electrode to be used repeatly to analyze for La^{3+}.

4.4 Conclusions

Reversibility of the complexation reaction in the modifying film is critical in allowing re-use of CMEs. Our results demonstrate that when a complexation reaction involves protons, a change in pH can be used to rapidly reverse complex formation, even when it appears irreversible in the film at the analytical pH.

The Auger depth profile results demonstrate two important features of the La•Q systems. The first is the evidence that mass transport of La^{3+} in the film, and not charge transport between redox sites, is the factor that dictates the requirement for thin films. The other relates to the mechanism of charge transport in the film. For electrostatically bound redox species it is difficult to determine whether site-site exchange of the electroactive species, or electron transfer through self-exchange, is the dominant mechanism of charge transport. In the case of the La•Q systems site-site exchange of the complex would lead to a uniform distribution of La^{3+} in the film, in contrast with the data obtained by Auger depth profiling, Figure (4-3a). Consequently, at least for the complex, the so-called electron hopping mechanism between redox species arising from electron self exchange must be the dominant form of charge transfer in the film.

A unique feature of the response of $[QPVP•Q]_{surf}$ films to La^{3+} is that the analytical response arises in part from the change in film transport properties as La^{3+} is extracted into the polymer film. The increase in D_{ct} could result from an increase in the self-exchange rate, k_e, for the complex relative to the ligand. However, based on the quasi-reversible nature of the cyclic voltammetry for the solution complex, Figure (3-1) in Chapter 3, a decrease in k_e is more likely. An increase in the mobility of the complex in the

film, due to the decreased charge of the complex relative to the free ligand, is a more likely cause of the increase in D_{ct} as $[La^{3+}]$ increases. The increase in mobility would then lead to enhanced site-site exchange, or more frequent collisions, resulting in increased rates of electron self-exchange. The latter suggestion is consistent with the Auger depth profile data, as discussed above.

In the design of modified electrodes for analysis of metal ions attention should be given to controlling permselectivity of the polymer matrix to reduce problems associated with substrate transport. This may be accomplished through increasing the solvent compatibility (swelling) of the film, varying the charge of the ionic sites, or by incorporating a high density of functional groups that can form labile complexes with the analyte, in addition to the presence of a strongly complexing analytical agent.

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Chapter 5 Effects of Added Plasticizer on Redox Ion Charge Transport in Quaternized Polyvinylpyridine Films

5.1 Introduction

Charge transfer rates through polymer films on chemically modified electrodes (CMEs) are fundamental to the behavior and application of such electrodes [1]. The overall charge transport process can be described by the laws of diffusion and its rate expressed as a diffusion coefficient for charge transport, D_{ct}, [2-4]. Electron transport through modifying polymer films is generally believed to involve electron-hopping reactions between redox centres and/or site-site exchange of redox species, depending on the nature of the redox sites and the polymer film. The overall mechanism and rate is governed by the electron self exchange rate between redox centres, and the diffusion coefficient for mass transport of the redox centre, which is related to mobility of associated solvent molecules in the film and segmental motion of the polymer chains [1,3,5].

Frequently, D_{ct} is at least two to three orders of magnitude smaller in the polymer film than the diffusion coefficient for the same redox couple in solution, and this

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limits the current density attainable for a given film thickness. As well, analytical applications of CMEs can require diffusion of analyte into the film and this may be hindered by low diffusion coefficients for mass transport, D_{mt} [6-10]. Increasing the extent of solvent swelling of the polymer matrix [11,12] or inducing heterogeneity in the polymer film through the use of polymer mixtures [13] are two methods that have been found to increase both D_{ct} and D_{mt}. Miller and Majda [14,15] have reported that lateral charge transport in bilayer assemblies can be increased in the presence of octanol in solution, and suggest this is due in part to increased fluidity of the bilayer when octanol is intercalated.

In this chapter we examine the use of a plasticizer in preparing quaternized polyvinylpyridine (QPVP) films, and its effect on D_{ct} for redox species ion exchanged into the film. Addition of plasticizer to a polymer is known to increase the mobility and flexibility of the polymer segments [16,17], and is a commonly used method to improve ionic conductivity in polymer matrices used in ion sensitive electrodes [18-21]. Through this effect, or by directly solvating redox ions in QPVP, it was expected that D_{ct} could be increased, this was found to be the case.

5.2 Experimental

Alizarin red S, alizarin complexone and α,α'-dibromo-p-xylene were used as received from Aldrich, as were dioctylphthalate (DOP) and dibromodecane from Eastman. Water was doubly distilled from alkaline permanganate. All other chemicals were reagent grade. Synthesis of 64% quaternized polyvinylpyridine (QPVP) has been reported in Chapter 4. Polyvinylpyridine (500,000 M.W.) was a kind gift from Reilly Tar and Chemicals.

Cyclic voltammetry was performed with a PAR 273 potentiostat, or a Pine RDE-4, and a Kipp and Zonen BD90 XY recorder. Chronoamperometry was performed with a PAR 273 interfaced to an IBM PC-XT as controller and data acquisition system. Glassy carbon electrodes were used as working electrodes, preparation and cleaning processes have been decribed in Chapter 3.

Modified carbon electrodes were prepared by allowing a methanol solution of the appropriate components to evaporate under a methanol atmosphere (~3 h) and then heat treating at 60°C (2 h) to promote cross-linking [6]. The cross-linking agent was always present at a constant molar ratio of 5:1, QPVP to reagent, which is sufficient to completely quaternize the remaining free pyridine. Free standing films were prepared by casting on Teflon substrates and the density of these films was determined in the dry state. The extent of

polymer swelling in aqueous solution was determined by measuring the thickness of free standing films with a micrometer before and after aqueous soaking for 20 min to 2h. Coatings of ~40 nm thickness on polished Si slides, and ~5 μm thickness on glass microscope slides, were also prepared by spin coating. A glass or Si slide was fixed on a spin motor and a methanol solution of the polymer composition was added, in a portion of 2 to 5 drops, to the surface of the slide, then the motor was turned on to spin off the solution. Time, about 15 seconds, was allowed for the solvent to get evaporated before another addition of polymer solution. After the coating process was completed, the slide was allowed to dry overnight at room temperature. The thickness of the dry polymer film and the change in thickness after aqueous exposure, pH 9.2, were determined by surface profilometry (Alpha Step Profilometer, Tencor Industries). Part of the polymer film was carefully removed from the slide with a razor blade so as to establish a sharp step and the height of this step was assumed to be the thickness of the polymer film. Thickness measurements of the wet polymer were much less precise than those of the dry material for both methods, possibly due to a decrease in polymer hardness.

Polymer coverage in moles of pyridine units/cm^2, Γ_{py}, was determined by cyclic voltammetry (10 mV/s) following extended ion exchange of $Fe(CN)_6^{4-}$ into the film at pH 2 (0.2 M trifluoroacetate buffer), assuming total charge compensation

by $Fe(CN)_6^{4-}$. The $Fe(CN)_6^{4-}$ was exchanged back out by exposing the electrode to 4 M KCl for 1.5 h or longer. The diffusion coefficient for charge transfer was determined by chronoamperometry and rotating disk voltammetry. A 0.1 M NaH_2PO_4/Na_2HPO_4 buffer at pH 7 was used for measurements involving $Fe(CN)_6^{4-}$, most of which were performed by R.Chemerika. A 0.1 M NH_4Cl/NH_4OH buffer at pH 9.2 was used as the supporting electrolyte for alizarin solutions. Coverage of redox ion, Γ_{Redox}, was measured by cyclic voltammetry (10 mV/s) immediately following the potential step. Experimental procedures for electrochemical measurements have been detailed in Chapter 4.

5.3 Results and Discussion

Addition of a plasticizing agent to a polymer commonly produces a composite with thermal and mechanical properties differing from the pure polymer [16,17]. Free standing films of 64% quaternized polyvinylpyridine (QPVP), with a constant amount of dibromoxylene as cross-linking agent sufficient to quaternize the remaining pyridine groups, and a variable amount of dioctylphthalate (DOP) added as plasticizer, were prepared to evaluate properties of the composite films. Films prepared with QPVP and dibromoxylene alone (type I) were very brittle, tending to shatter when handled or cut. Following 24 to 48 h exposure to aqueous solution, pH 7, such

films were solvent swollen and had broken up into many smaller pieces. Films were also prepared with DOP added at a 0.5:1 molar ratio of DOP to moles of pyridine moieties (type **II**), and a 1:1 DOP to pyridine unit molar ratio (type **III**). The same amount of cross-linking agent was added to plasticized membranes as to unplasticized QPVP films. Both compositions **II** and **III** gave flexible free standing films that were durable during handling and were easily cut into smaller pieces without damage. Such films appeared to swell less than type **I** films after 24 to 48 h exposure to aqueous solution, and did not break apart or lose mechanical strength.

The densities of the different film compositions were determined for dry films, Table (5-1). The film composition following solvent evaporation was assumed to be that of the casting solution. The results show that the film density increases with addition of DOP. However, Table (5-1) shows that the molar density of the total number of pyridine sites in the composite films decreases with addition of DOP, indicating the contribution from the partial molal volume of DOP is significant.

To evaluate the effect of solvent swelling, films were prepared on solid substrates and their thickness was determined by profilometry before and after soaking in aqueous solution. Within experimental error there was no difference in swelling for the three compositions following

Table (5-1). Density of QPVP and Plasticized Films

composition	molar ratio[a]		density	molar density[c]
	QPVP[b] / diBr	DOP / QPVP	g/cm^3	mmol/cm^3
I	5	0	0.58	2.4
II	5	0.5	0.68	1.6
III	5	1	0.81	1.3

(a) Molar ratio of components in film casting solution, expressed relative to the moles of total pyridine sites.

(b) diBr is dibromoxylene.

(c) In terms of total number of pyridine sites.

soaking for 20 min to 2 h, although as noted above extended exposure to aqueous solution swells pure QPVP films more than the other compositions. An increase in thickness of 15-25% was observed for ~40 nm thick films after 20 min to 2 h soaking, and ~5 μm thick films on Si showed an increase of 10-20%. Free standing films of 0.1 to 0.2 mm thickness also showed a 10-25% increase for all three films. Due to poor precision in determining wet film thickness the values of D_{ct} were calculated using the density of the dry films. Since electrodes were studied within the first half to four hours of exposure to solution all compositions would be expected to have swelled to about the same extent.

The effect of added plasticizer on D_{ct} in QPVP films was examined for three redox systems, $Fe(CN)_6^{4-}$, alizarin red S (ARS), and alizarin complexone (AC), at pH values of 7 and 9.2. The coverage of QPVP expressed as the number of pyridine moieties, Γ_{py}, was in the range 1.4×10^{-8} to 2.2×10^{-7} mol/cm^2. The coverage of redox anions incorporated in the films varied from 0.22 to 2.2×10^{-8} mol/cm^2 for $Fe(CN)_6^{4-}$ and 0.26 to 6.8×10^{-8} mol/cm^2 for the alizarin derivatives. A decrease in D_{ct} was observed as the coverage of redox anion increased for a given value of Γ_{py} as is commonly observed for other systems. This is believed to result from the effects of ionic cross-linking on mobility in the polymer matrix [1,3,5]. The data presented in Table (5-2) was obtained for a range of values of the ratio $\Gamma_{Redox}/\Gamma_{py}$, but is given as an

average for all ratios to indicate the general trend induced by addition of plasticizer. The range of D_{ct} values obtained for a given polymer composition and redox ion were treated by calculating the standard error of the mean to the 95% confidence limit given by equation (5.1) [23]:

$$\mu - \bar{x} = \pm ts/\sqrt{n} \qquad (5.1)$$

where μ is the true mean, $\bar{x}$ and s are the experimental mean and standard deviation respectively, n is the number of measurements, t is the value of Student's t for the 95% confidence interval, and $ts/n^{1/2}$ is the standard error for that interval. Using the Kolmogorov-Smirnov test [24] the data was found to obey a normal distribution, indicating the above analysis is appropriate.

The value of D_{ct} for $Fe(CN)_6^{4-}$ in polyvinylpyridine and partially quaternized QPVP is typically 0.5 to 1 x 10^{-8} cm^2/s at low pH [3,22], where the free pyridine sites are protonated and the polymer is apparently more swollen with H_2O [9]. At pH 7 D_{ct} in the nearly fully quaternized films used in this study is 8.0 $\pm$ 3.6 x 10^{-10} cm^2/s. Although the accuracy of these D_{ct} is questionable, the precision is not. The data in Table (5-2) shows that when an equimolar ratio of pyridine sites to DOP is used D_{ct} for $Fe(CN)_6^{4-}$ in the film is increased about fivefold. Comparison of the standard error of the means indicates the change in D_{ct} is statistically significant for a 1:1 ratio. However, for a DOP to pyridine site ratio of 0.5:1 the values of D_{ct} do not

Table (5-2). Effect of Plasticizer on D_{ct} in QPVP Films

Redox anion	Polymer[a] Composition	Number of Observations	% coverage[b] range	D_{ct}[c]	standard error[d]
$Fe(CN)_6^{4-}$[e]					
	I	10	30-60	8.0	3.6
	II	5	30-45	13	5.6
	III	19	25-40	38	11
ARS[f]					
	I	28	10-70	1.6	0.4
	II	28	15-80	2.0	0.5
	III	34	15-40	3.3	0.7
AC[f]					
	I	31	35-95	0.5	0.1
	II	31	30-75	1.2	0.3
	III	31	25-75	1.7	0.3

(a) Polymer compositions as in Table (5-1).

(b) % of pyridinium sites charge compensated by redox anion.

(c) in 10^{-10} cm^2/s

(d) The precision of the mean expressed as the standard error within 95% confidence limits, in 10^{-10} cm^2/s.

(e) Measured by potential step from -0.3 to +0.6 V vs SCE in 0.1 M phosphate, pH 7.0

(f) Measured by potential step from -0.4 to -1.1 V vs SCE in 0.1 M NH_4Cl, pH 9.2.

differ at the 95% confidence interval, although they are statistically different at the 90% interval. This may in part reflect the fact only 5 measurements were made for the type II film.

The alizarin derivatives differ considerably from $Fe(CN)_6^{4-}$ in being fairly large anions with a potential for hydrophobic interaction with the plasticizer, and in the case of AC in having well separated charge sites. The charge on these ions at pH 9.2 is 2^- for ARS [25], and about 80% 2- and 20% 3^- for AC [26]. These quinones can be used in the analysis of La^{3+} by ion exchange into QPVP films as we have recently shown [6]. They are similar in many respects to other complexing ligands that have been bound in modifying films for electroanalysis [7-9]. The data in Table (5-2) show both ARS and AC exhibit a statistically significant increase in D_{ct} for composition III versus films with no plasticizer (type I), with D_{ct} increased by a factor of about 2 for ARS and 3.5 for AC. For composition II both ARS and AC show an increase in D_{ct} over composition I, however, the increase is not significant within the 95% confidence interval for ARS while it is for AC. The addition of plasticizer appears to have little other effect on the quinone redox processes, the peak potentials do not change, and the number of electrons in the reduction also remains unchanged. This indicates that the polymer film environment

remains relatively unchanged despite the large amount of hydrophobic plasticizer added.

The effect of added DOP on metal complexation by ARS and AC in QPVP films was also examined. We have previously reported that La^{3+} is complexed by both quinones in QPVP, resulting in 150 to 200 mV shifts in peak reduction potential for the ligands [6]. However, difficulties with poor mass transport of La^{3+} in the film require that QPVP films be no more than 30Å thick and result in a detection limit of about 0.1 mM La^{3+}. Using a 1:1 ratio of pyridine sites to DOP, with cross-linking reagent also added, polymer film thicknesses of ~100Å still respond to La^{3+} in the manner of the thinner composition I films. More importantly, the presence of La^{3+} can be determined at concentrations of 20 μM, indicating improved extraction and transport of the metal ion in the polycationic matrix. The results are consistent with an increase in D_{mt} for La^{3+} in the plasticized film. However, the peak current measured by differential pulse voltammetry only increases very slightly as La^{3+} ion concentration increases. The results in Chapter 4 show that the electrode response is related to the change in mass transport properties when La^{3+} is extracted into the unplasticized polymer film. The independence of peak current on $[La^{3+}]$ may be due to the complexation reaction causing much less change in the mass transport properties of the plasticized films, due to their improved transport characteristics.

The Dahms-Ruff equation has been shown to describe D_{ct} at least qualitatively in polymer films [27,28]. Following Buttry and Anson [28] this relation can be expressed as

$$D_{ct} = D_{mt} + D_{et} = D_{mt} + \pi\partial^2 C/[4(1/k_d+1/k_{ex})] \qquad (5.2)$$

where D_{et} is the diffusion coefficient for the electron hopping or self exchange process. D_{et} depends on the distance between redox sites at which electron transfer occurs ∂, the redox site concentration C, and the apparent electron self-exchange rate in the polymer film which itself depends on the true electron self-exchange rate k_{ex}, and the diffusion controlled rate constant k_d. The magnitude of k_d can be estimated by the Smoluchowski equation and is directly proportional to D_{mt} [28,29], indicating that even when D_{et} is larger than D_{mt} the value of the diffusion coefficient for charge transport can still be strongly dependent on the mass transport rate of the redox ion in the film. This dependence arises since motion of the redox sites must occur to allow the species to attain sufficient proximity for electron transfer to occur [1].

The above discussion is important since we [6] and others [30] have recently shown that electron hopping plays a dominant role in charge transport by ARS and AC in polycationic films. However, equation (5.2) shows that the increase in D_{ct} for the redox couples studied, and the apparent increase in D_{mt} for La^{3+} with added plasticizer, can

easily be interpreted in terms of an increase in mass transport rates even when D_{et} is dominant, since D_{et} is a function of D_{mt}. An increase in the intrinsic self-exchange rate k_{ex} with added DOP cannot be ruled out, although the similarity of the change in D_{ct} for both $Fe(CN)_6^{4-}$ and the quinones, which are very dissimilar redox couples, suggests this is not the case.

Increased mass transport rates in the presence of DOP could arise from an increase in solvation of the redox ions, although the relatively poor solvation of ions by the ester argues against this. Another possibility is that the decrease in pyridinium site density with added plasticizer results in less effective ionic cross-linking. However, the expected decrease in dielectric strength of the matrix with added DOP would enhance ion pairing with the fixed pyridinium sites, and it is difficult to predict the net effect. The most likely cause for increased transport rates is an increase in the mobility and flexibility of the polymer chain segments. This is a well recognized effect of using plasticizers, and polymer segmental motion has been identified as an important factor in charge transport [1-5]. When D_{et} is important the rate of collisions resulting in electron transfer can be controlled by segmental motion of the polymer [1,5], or the viscosity of the polymer matrix. For the more bulky alizarin complexone anion it is possible that both an increase in solvation of AC and the polymer

chain segments by added DOP may occur. These combined effects could be responsible for AC showing a more significant increase in D_{ct} at a lower degree of plasticization than do ARS or $Fe(CN)_6^{4-}$.

5.4 Conclusion

Addition of plasticizer to quaternized polyvinylpyridine film increases the charge transport rates of redox ion in the film. Plasticized-QPVP electrodes incorporated with alizarin derivatives respond to La^{3+} at a concentration of 20 μM. However, the electrode response does not show a significant La^{3+} ion concentration dependence as compared to unplasticized films. Since the plasticized film shows improvement in flexibility, the change in mass transport properties upon complexation to La^{3+} may not have a significant impact on the plasticized films.

In addition to increasing charge transport rates the presence of plasticizer decreases the solvent swelling and increases the durability of the polymer film. This should be of significant benefit, since even with an added cross-linking agent QPVP films on C electrodes tend to slowly dissolve when stored in aqueous solution over several days, unless an electrostatic cross-linking agent such as $Fe(CN)_6^{3/4-}$ is present. Perhaps more interesting is the possibility of enhancing selectivity of complexing ligands

incorporated in the polymer film by judicious choice of the plasticizer. For polyvinylchloride based ion selective electrode membranes the choice of plasticizer can alter the selectivity of the ion carrier [19-21]. Significant effects can arise from relatively subtle changes in the plasticizer, such as found for neutral carrier based Na^+ electrodes for which the use of dioctyladipate rather than dioctylsebacate leads to higher selectivity for K^+ than Na^+ [20]. Whether such effects on complexation can occur in a more polar matrix such as QPVP is not known.

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Chapter 6 Conclusions and Future Work

As shown in previous chapters, polymer-modified electrodes sensitive to La^{3+} concentrations can be prepared by ion exchanging either alizarin red S or alizarin complexone into quaternized polyvinylpyridine films. Electrode response is related to the changes in polymer crosslinking upon complexation and limited by the permeation of La^{3+} through QPVP films. Results suggest that electron-hopping is the dominant route for charge transport in QPVP films. Plasticized QPVP films show an increase in the diffusion coefficient for charge transport of redox ions over unplasticized ones. Although plasticized films show responses to La^{3+} at much lower concentration when compared with unplasticized films of similar thickness, the dynamic range for electroanalysis of La^{3+} ions actually decreases. The alizarin-modified electrodes do not show much increase in current measured by differential pulse voltammetry when La^{3+} ion concentration increases. This may be because the change in mass tranport characteristics in the plasticized films upon complexation with La^{3+} is insignificant; these films have already shown improved polymer flexibility and transport properties.

Future work

The mass transport of the substrate and the charge transport of redox anions in the polycationic film play very important roles in controlling the electrode behavior. The La-sensitive electrodes we developed can be used as a tool to examine these transport processes in different polycationic films. Future work would examine polymer systems with a greater extent of solvent swelling and permeability. Montgomery and Anson [1] have prepared a copolymer with both hydrophobic styrene groups and hydrophilic quaternized amino styrene groups and found that mixtures of this copolymer and other homo-polyelectrolytes such as polyvinylpyridine gave stable electrode coatings. A very high diffusion coefficient of charge transport for $Fe(CN)_6^{4-}$ in these composite films, on the order of 10^{-6} cm^2/s, was reported and the result was related to the internal morphology of the composite polymer films. Unfortunately, our attempts to synthesize the same copolymer gave a material that did not show similar charge transport properties when mixed with polyvinylpyridine. Van Koppenhagen and Majda [2,3] also reported the synthesis of a structurally heterogeneous electrode films of acrylamide/vinylpyridine gels which gave high transport rates. The gels were synthesized in aqueous solutions and thin films of the dried copolymer were cut by microtome and placed on carbon electrodes. Unfortunately, we experienced some technical difficulties in following their procedure to

obtain thin copolymer films and place them on carbon electrodes.

The gel film approach is attractive, however, and it should prove possible to synthesize polymer gels that could be cast from solution directly onto the electrode. This would eliminate the difficulties associated with Majda's approach of transferring ready made films to the electrodes. One approach is to synthesize an acrylamide/vinylpyridine/vinylacetate copolymer through radical polymerization. The acetate functionalities could be selectively reduced by $NaBH_4$-$AlCl_3$ [4] and then reacted with crosslinking reagents. The resulting product could be applied to electrode surfaces in solution form to give a copolymer gel with transport properties similar to the acrylamide/vinylpyridine copolymer gel prepared by Van Koppenhagen and Majda. We, as well as others, have used very thin polyvinylpyridine-based films in electroanalysis of different species such as La^{3+}, Fe^{3+} [5] and $Cr_2O_7^{2-}$ [6]. Gehron and Brajter-Toth [7] have empolyed thick QPVP films (up to ~ 2 μm) crosslinked with bathophenanthroline-disulphonic acid in electroanalysis of Fe^{2+} ions. The differing responses of these polymer-modified electrodes are very likely related to their transport phenomena. The copolymer proposed above could be used to examine the transport characteristics in relation to these systems. Better understanding of the transport processes is of

fundamental importance in using chemically modified electrodes as an analytical tool.

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